

APPLICATIONS OF A RUTHENIUM CATALYST IN ACYCLIC DIENE
METATHESIS (ADMET) CHEMISTRY: DEPOLYMERIZATION AND
POLYOLEFIN MODELLING STUDIES

By

MARK D. WATSON

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Abstract of Dissertation Presented to the Graduate School
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Mark D. Watson

May 1999

Chairman: Kenneth B. Wagener
Major Department: Chemistry

Investigation of the utility of Grubbs' ruthenium carbene, $\text{Ru}(\text{CHPh})(\text{PCy}_3)_2\text{Cl}_2$, as a catalyst for various operations of Acyclic Diene Metathesis (ADMET) chemistry is presented. Applications include the metathesis depolymerization of cis-1,4-polybutadiene, ADMET polymerization of functionalized dienes, and tandem metathesis/hydrogenation reactions in which the ruthenium complex serves to catalyze both reactions.

In Chapter 3, the unprecedented stability of the ruthenium complex in the presence of ethylene is exploited for effective depolymerization of 1,4-polybutadiene by cross-metathesis with ethylene. Vastly improved yields of hexadiene over those previously reported utilizing well-defined early transition metal complexes were

realized. The first accounts of the remarkable ability of the ruthenium complex to effect the solvent-free depolymerization of 1,4-polybutadiene and its application in the synthesis of end-functionalized polymers are also disclosed.

In Chapter 4, the dual utility of the catalyst for both olefin metathesis and hydrogenation is described. Adsorption of the catalyst residue on the surface of silica gel converts it to a heterogeneous system, which is effective for catalytic olefin hydrogenation at room temperature and moderate pressures. The two reactions may be conducted in tandem to produce saturated polymers, including telechelic polyethylene. Further application of the tandem process for C-C bond construction in small molecule synthesis is described.

In Chapter 5, the metathesis/hydrogenation process disclosed in Chapter 4 is exploited for the production of model periodic ethylene copolymers. A homologous series of symmetrical dienes with varied central pendant functionality were synthesized to this end. ADMET polymerization of these monomers and subsequent hydrogenation yielded periodic models for copolymers of ethylene with vinyl acetate, vinyl chloride, acrylates, and styrene. Thermal analysis of the resulting polymers revealed the predicted relation of increasing melting point with increasing ethylene run length. Within a series of polymers with identical ethylene run lengths, increasing steric bulk of the regular pendant functionality resulted in greater melting point depression.

CHAPTER I INTRODUCTION

The now continuous stream of advances in polymer chemistry attending new developments in catalytic organometallic chemistry¹ can generally be classified into two categories: (1) original chemical transforms and (2) the betterment of known chemical transforms. The latter class may be manifestations of improved catalyst efficiency, chemoselectivity, broader scope to encompass substrates with diverse functionalities, and resistance to ubiquitous trace poisons allowing more practical implementation.

The subject of this dissertation, which falls into the second category above, involves the exploitation of unique properties of a well-defined ruthenium metathesis catalyst to improve upon and expand the scope of various applications of Acyclic Diene Metathesis (ADMET) chemistry. One aspect of the studies focussed on ADMET depolymerization where the resilience of the catalyst was exploited for improved conversions in reactions involving ethylene as a substrate. Also the first, to the best of our knowledge, "solid state" depolymerizations of ultra-high molecular weight polybutadiene catalyzed by a discrete metathesis catalyst were performed. Exciting observations were made regarding the dual-purpose use of the catalyst for post-metathesis hydrogenation chemistry, made possible by the nature of the late-transition metal center. The timing of these observations coincided with the growing implication of metathesis polymerization in tandem with hydrogenation as a powerful method for

macromolecular engineering. This prompted the development of a facile process for the production of periodic model ethylene copolymers involving homogeneous metathesis in tandem with heterogeneous hydrogenation.

To facilitate cohesive presentation, the somewhat disparate subjects of depolymerization, hydrogenation, and model polymer engineering are apportioned into chapters 3, 4, and 5, respectively. The remainder of this chapter will serve to briefly introduce the metathesis reaction and advances in catalyst development pertinent to the establishment of the ADMET reaction as a viable synthetic scheme. The ADMET reaction, which is the unifying concept common to all the studies reported herein, deserves separate discussion for adequate understanding of the subject matter.

The Olefin Metathesis Reaction

The olefin metathesis reaction is a powerful organic transform, which formally divides olefinic compounds at the carbon-carbon double bonds into carbene fragments and then redistributes them, forming new olefins.² The process is catalyzed by a metal carbene complex which may be preformed or formed *in situ*, and may be homogeneous, heterogeneous, or supported on an insoluble substrate. The key steps in the mechanism are shown in Figure 1-1. Coordination of a substrate olefin to the metal center leads to the formation of a metallocyclobutane. Cleavage of this ring may occur either along the vertical or horizontal leading to, respectively, starting materials or a new olefin and new metal carbene. The olefin product may be *cis*, *trans* or a mixture as determined by the steric demands of the substrate and the choice of catalyst. In the special case where $R = R''$, termed degenerate metathesis, no new products are formed in the forward reaction.

The mechanism finds analogy in the Wittig reaction, shown for comparison in Figure 1-1, where a carbene fragment is delivered to a carbon doubly bonded to oxygen forming a new C=C bond. A major difference between the two mechanisms lies in the reactivity of the other doubly bonded product liberated upon cleavage of the cyclic intermediate. In contrast to the Wittig reaction, the new metal carbene formed in the metathesis reaction can repeat the reaction with any other reactive C=C bond.

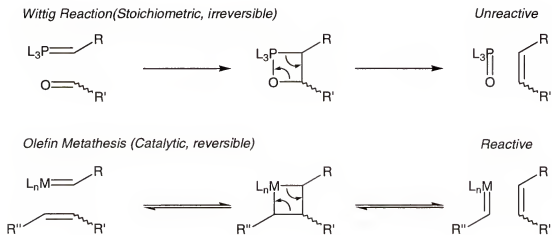
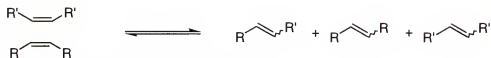


Figure 1-1. Key steps of the olefin metathesis reaction compared to the Wittig reaction.

The olefin metathesis reaction may be divided into categories² depending on the structure of the starting materials and products as depicted in Figure 1-2. Regardless of the particular pathway, it is now widely accepted that each of these processes has as common intermediates the metal carbene and the metallocyclobutane. In the simplest case of a single symmetrical olefin, the substrate will be isomerized to an equilibrium mixture of cis/trans stereoisomers via repetitive degenerate metathesis. For an unsymmetrical olefin substrate or a mixture of different starting olefins of similar reactivity, the result is a statistical redistribution of carbene fragments upon reaching

equilibrium. Following Le Chatelier's Principle, removal or addition of any of the reactants or products may shift the position of the equilibrium.

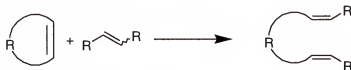
Acyclic



Ring Opening Metathesis Polymerization (ROMP)



Ring Opening Cross-Metathesis



Ring Closing Metathesis (RCM)



Acyclic Diene Metathesis Polymerization (ADMET)



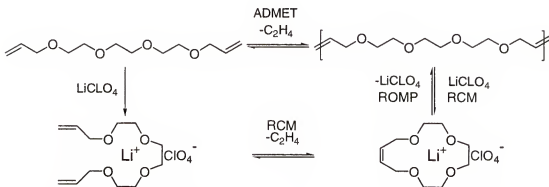
Figure 1-2. Classifications of olefin metathesis reactions.

By ring opening metathesis polymerization (ROMP), cyclic olefins may be converted to high polymer via a chain process provided the energetics are favorable. The process is thermodynamically favored for 3-, 4-, 8-, and larger membered rings but is unfavorable for cyclohexene due to stability of the six-membered ring. Cyclic olefins may also be ring opened to monomeric compounds by cross-metathesis of cyclic and

acyclic olefins. This “arrested ROMP” reaction occurs when cross-metathesis of the newly formed metal carbene from either the cyclic or acyclic olefin is favored over self-metathesis.

Conversely, compounds with more than one double bond appropriately spatially disposed may be cyclized by ring closing metathesis (RCM). This particular transform has been extensively exploited for the preparation of fine chemicals and extended to complicated natural product syntheses. Dienes may also be condensed intermolecularly to polyenes and high polymers by acyclic diene metathesis polymerization (ADMET), to be discussed in detail later. Competition between RCM and ADMET often exists, and its outcome may be governed to varying degrees by altering reaction conditions. The most significant variable is concentration, where dilute conditions favor intramolecular (RCM) reaction and bulk conditions favor intermolecular (ADMET) reaction. Chemical characteristics that hold the double bonds in close proximity, such as bulky groups between the olefins (Thorpe-Ingold Effect) and intramolecular hydrogen bonding may augment cyclization of dienes at the expense of linear products.³

Recently, Grubbs reported⁴ an elegant study in which ADMET, RCM, or ROMP could be driven in high conversion from the same olefinic substructure depending on reaction conditions as shown in Figure 1-3. Under bulk conditions, the oligoether diene was condensed to high polymer by ADMET. Introduction of an appropriate metal cation to a solution of either the polymer or the monomeric diene leads to hapto-coordination of the ether oxygens to the cation, bringing sequential olefins into proximity favoring RCM. The resulting crown ether could be obtained either from the diene or from high polymer



Development of the Olefin Metathesis Reaction

The history of the reaction parallels other catalytic processes such as Ziegler-Natta polymerization where obvious technical utility spurred almost immediate commercial exploitation preceding a fundamental understanding.² The reaction found application in the interconversion of hydrocarbon streams, diversifying olefin-manufacturing processes. These processes typically used empirically developed heterogeneous catalysts where a transition metal precatalyst was loaded onto an inorganic support and pretreated to generate the active catalyst, the structure of which was unknown. Two such processes^{2,5} that were developed by Phillips Petroleum Co. are depicted in Figure 1-4. The Phillips triolefin process, implemented in 1966, utilized metathesis to convert propene to ethylene and but-2-ene. In 1969, the Neohexene process was initiated, where neohexene is generated from ethylene and 2,4,4-trimethylpent-2-ene.

In spite of these early commercial applications of the process, it was not until the beginning of the 1970's that fundamental research resulted in proposal of the now-accepted mechanism⁶ (cf Figure 1-1) involving the key intermediacy of metal carbenes and metallocyclobutanes. The reaction became the subject of a number of research programs, both academic and applied, where the reasons for fundamental investigation were manifold.⁷ The initial commercial catalyst systems required excessive temperatures for practical activity, limiting the substrates to those with functionality that could withstand the harsh conditions. Application was also limited by low tolerance of the catalysts to Lewis basic functionality.⁸ In addition, lack of insight into the mechanism prohibited prudent catalyst engineering.

Phillips Triolefin Process



Neohexene Process



Figure 1-4. Early commercial applications of the olefin metathesis reaction.

Specific refinements were necessary to make the metathesis reaction a more general tool: (a) The catalyst must promote only one reaction (metathesis) with olefins; (b) the catalyst must tolerate and remain inert to other functionality (c) the catalyst should be active under milder conditions. Refinement in these aspects continues today through variation in the choice of the metal center, cocatalysts, and ligand environment.

Early catalysts were two part systems most commonly based on Mo, W, and Re activated by a main-group metal alkyl cocatalyst⁹ such as Al and Zn alkyls. The cocatalysts may serve more than one functions such as: A) provide alkyl ligands via transmetallation which can rearrange to the alkylidene by elimination processes, B) act as a ligand, modifying electron density of the transition metal through, for example, coordination to oxo and halo ligands. Due to their high Lewis acidity, some cocatalysts initiated side reactions via electrophilic reaction with C=C bonds. This shortcoming was overcome with the realization of cocatalysts with diminished Lewis acidity such as those based on Pb^{10a,b} and Sn^{10c-f}. Byproducts of a given catalyst system might also induce deleterious chemistry as in the case of WCl₆/Me₄Sn which generates HCl.²

Greater functional group tolerance was realized with the development of catalysts based on late transition metals.⁸ The late transition metals are softer Lewis acids and as a result, metathesis catalysts derived from these are more selective towards olefin groups in the presence of polar functionality. Heterogeneous systems based on Re have been studied extensively¹¹ and have proven to be more tolerant of functionality than early transition metal species. Though the process has yet to achieve commercial success, heterogeneous Re systems have been proven effective for the metathesis of unsaturated esters.

Well-Defined Metathesis Catalysts

Research efforts aimed at delineating the mechanism of the olefin metathesis reaction shifted towards the development of active preformed metal carbenes. Although stable isolable metal carbenes were reported as early as 1964 by Fischer, these species

proved to be inactive for metathesis.¹² The first isolable, metathetically active carbene complex was reported in 1974¹³ and shown to effect the ROMP of cyclooctene shortly thereafter¹⁴. This complex, $\text{CO}_5\text{W}=\text{CPh}_2$, required activation for metathesis through loss of a CO ligand induced by heating or UV irradiation but still represented a significant advance as the necessity for cocatalyst was eliminated.

Various researchers subsequently secured their place in the history of this drive to obtain well-defined metathesis catalysts, but most were to be overshadowed by the names Schrock and Grubbs. The former prepared the first class of highly active species based on W and Mo systems which were soon complemented by the Ru systems of Grubbs, to be discussed later.

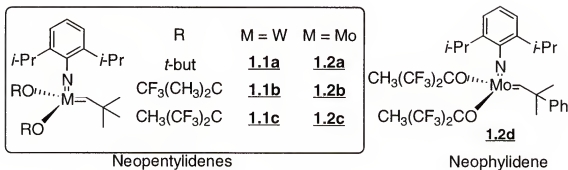


Figure 1-5. Well-defined, highly active W(VI) and Mo(VI) alkylidenes.

Through systematic variation of ligand environment, Schrock eventually developed a series of four-coordinate W(VI) and later Mo(VI) alkylidenes with tunable reactivity, shown in Figure 1-5. The bulky imido and alkoxy ligands serve in one fashion to diminish bimolecular catalyst decomposition while still allowing the approach and coordination of olefinic substrates. Variation of the steric and electronic nature of the alkoxide ligands allows the reactivity of the metal alkylidene to be engineered to differing

degrees, with highest reactivity observed for $R = \text{CH}_3(\text{CF}_3)_2\text{C}$, or hexafluoro-*t*-butoxy. For example, catalyst **1.1a** is effective for ROMP but not acyclic chemistry while **1.1c** not only catalyzes ROMP but is highly active for acyclic metathesis ($\text{TON} = 1000 \text{ min}^{-1}$ for 2-pentene). While representing a landmark advance in catalyst development, the W analogues still suffered from low tolerance to functionality. For example, although catalyst **1.1c** effected the metathesis of methyl oleate, catalyst lifetime was limited by deactivation via Wittig-type reaction with the ester carbonyl group.

The less electrophilic molybdenum analogues proved to be more tolerant of functionality and became the vehicle by which olefin metathesis was transformed into a trustworthy synthetic tool. The Mo catalysts' improved chemoselectivity has allowed the ROMP, RCM and acyclic metathesis of substrates containing a broad range of functionality including halo, ether, amine, amide, ester, thioether, and metal containing groups.¹⁵ The neophylidene complex **1.2d**, although no more effective than the neopentylidene analogue, is more easily prepared and therefore preferred.

Utilization of these catalyst systems for ROMP chemistry offers several advantages in addition to greater mechanistic insight. They allowed the preparation of a broad range of polymers in living fashion with predictable and narrow PDI's as well as block copolymers with well-defined block lengths.¹⁵ Also mild reaction conditions together with well-delineated reactivity minimized defects in the polymer microstructure. The Mo catalysts are still sufficiently oxophilic to react with aldehydes and ketones in a Wittig fashion, and this particular reaction has been capitalized upon for stoichiometric cyclizations of unsaturated carbonyl compounds¹⁶ and for end-capping of living ROMP reactions as shown in Figure 1-6. If functionalized benzaldehydes are used as end-

capping reagents in ROMP reactions, polymers with narrow polydispersity and useful end-groups can be obtained.¹⁷

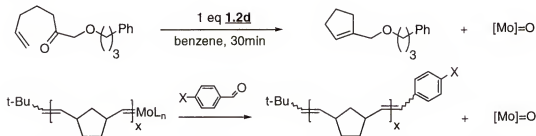


Figure 1-6. Reaction of Mo alkylidenes with carbonyl-containing substrates: Ring-closing olefination¹⁶ and end-capping of living ROMP¹⁷.

As mentioned previously, these catalyst systems would soon be overshadowed by well-defined ruthenium catalyst systems which are superior in many aspects. Schrock's W and Mo alkylidines, like their ill-defined predecessors based on early transition metals, still displayed moderate functional group tolerance. They are easily deactivated by compounds containing active hydrogens (acids, alcohols, H_2O , etc) and oxygen. Their widespread usage is also limited by thermal instability during storage and expense of preparation.

Ruthenium Metathesis Catalysts

The promise of ruthenium systems as robust, functional group tolerant catalysts was foreshadowed during the first stages of development of the metathesis reaction, where RuCl_3 was shown to be effective for the ROMP of cyclobutenes and norbornene in aqueous and alcoholic environments.² Polynorbornene has been produced commercially for over 15 years in a process utilizing RuCl_3 in alcohol solvent and the reaction is even

promoted by the presence of oxygen. However, utility is limited to ROMP of high strain ring systems.

In 1992, reports began to emerge of the *in situ* activation of ruthenium complexes for ROMP by addition of diazo compounds.¹⁸⁻²⁰ Activation occurred presumably via the formation of ruthenium carbenes, the presence of which was supported by NMR studies. Initial studies¹⁹ with diruthenium (II) tetracarboxylates activated by ethyl diazoacetate were limited to high strain olefins and suffered from competing cyclopropanation of the olefin substrates. This observation finds precedent in extensive studies of transition metal catalyzed cyclopropanation, which is most effective with diazocarbonyl compounds.²¹ Ethyl diazoacetate may be used to activate $\text{Ru}(\text{H}_2\text{O})_6(\text{OTf})_2$ for the ROMP of cyclooctene, which also indicates that the difficulty in polymerizing the low strain monomers with Ru(II) complexes lies not in propagation but in initiation.²⁰

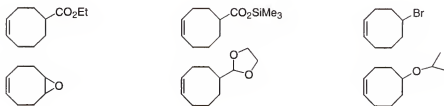


Figure 1-7. Functionalized cyclooctenes polymerized via ROMP catalyzed by $[\text{Ru}(\text{p-cymene})_2\text{Cl}_2]_2 + \text{PCy}_3 + \text{trimethylsilyldiazomethane}$.

A variety of ruthenium complexes have been studied, with relative success reported¹⁹ for the type $[\text{Ru}(\text{arene})_2\text{Cl}_2]_2$ activated by trimethylsilyldiazomethane (TMSD) both with and without added trialkyl phosphines. These multicomponent systems have been applied to the ROMP of various functionalized norbornenes, oxanorbornenes, and cyclooctenes. Each of the functionalized cyclooctenes shown in Figure 1-7 were

polymerized to high molecular weight ($M_n = 5 - 12 \times 10^4$ g/mol, PDI = 1.4 – 2.2) in good to moderate yields.

Discrete Ruthenium Carbene Complexes

While these multicomponent ruthenium systems enabled the metathesis of substrates with a variety of functionality not previously possible with other transition metals, concurrent developments in the synthesis of related preformed ruthenium carbenes would come to virtually dominate the attention of the metathesis community.^{8,22} The first preformed ruthenium species which were highly active for acyclic metathesis were reported²³ in 1993 and an improved version²⁴, **1.4**, followed shortly thereafter (Figure 1-8). While other versions were prepared with differing phosphine and carbene ligands, **1.4** is preferred as its synthesis is extremely facile, utilizing diazo compounds similar to the process described earlier for *in situ* activation of ruthenium complexes. In addition, **1.3** has been shown to be a slower initiator due to the greater stability of the more highly conjugated vinylidene relative to the benzyldiene.



Figure 1-8. Discrete ruthenium carbene olefin metathesis catalysts.

While it is certain that the continually growing knowledge base will lead to ever-increasingly effective catalysts, the explosion of applications made possible by this series of Ru carbenes makes them seem the current zenith. Their technical and synthetic value

has sparked a flurry of research efforts aimed at more facile catalyst preparations, which now approach the degree of difficulty of sophomore organic chemistry laboratory exercises.

Some of the outstanding features of the catalysts are as follows. They can be employed in both aqueous^{25,26} and alcoholic solutions²³. The unprecedented stability of the catalysts to adventitious moisture and other typical poisons enables their practical use without highly specialized equipment, and they may be stored for long periods of time in air without decomposition. The practical organic chemist has only to sparge a simple reaction vessel, the substrate and any solvents with nitrogen before reaction. The catalyst **1.3** has been used for RCM of dienes containing aggressive functionality such as OH, CO₂H, aldehyde and amide groups²⁷ (Figure 1-9). These transforms are impossible with early transition metal catalysts due to intolerance of the catalysts to these functionalities.

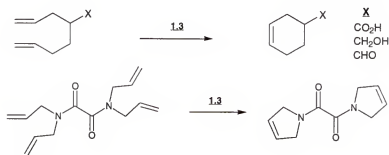


Figure 1-9. RCM of dienes with aggressive functionality.

It should be noted however that the success of the reactions in Figure 1-9 does not show that the complex is impervious to these functionalities, but rather the catalyst is sufficiently tolerant to allow good yields of product when the kinetics of the desired reaction (e.g. RCM) are sufficiently rapid to compete with any deleterious side reactions. The success of a metathesis reaction in the presence of these functionalities therefore

depends on the substrate under study. For instance, while hydroxy-functionalized substrates may be employed successfully in ROMP and RCM schemes, dimerization of acyclic ω -alkenol alcohols gives poor yields and some isomerization of the alcohol substrates to aldehydes due to slower kinetics of acyclic chemistry.²⁸

While catalysts **1.3** and **1.4** are much more tolerant to oxygenated groups, they are less effective than early transition metal complexes for the metathesis of sulfur²⁹ and phosphorous³⁰ containing substrates. This can be explained in terms of hard-soft theory where the softer S and P atoms more effectively complex the soft ruthenium center than the harder earlier transition metal centers. Catalyst **1.4** has, however, been proven effective³¹ for the first ever RCM reaction of phosphonate compounds as shown in Figure 1-10.

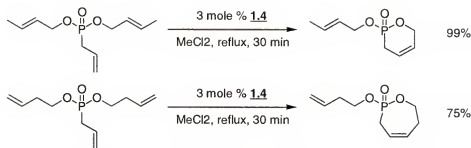


Figure 1-10. RCM of dienes with phosphonate functionality catalyzed by **1.4**.

Complexes **1.3** and **1.4** have promoted the affirmation of the metathesis reaction by the synthetic community, where growing confidence is indicated by the willingness to incorporate the reaction as a transform in advanced stages of multi-step synthetic sequences.³ The most common application is ring closure, noteworthy examples³²⁻³⁴ of which are shown in Figure 1-11.

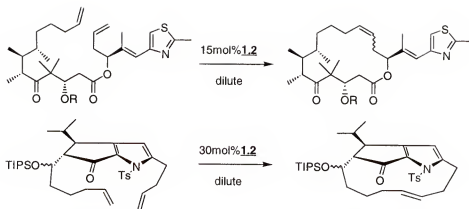


Figure 1-11. Applications of RCM catalyzed by **1.4** in multistep synthesis.

Acyclic Diene Metathesis (ADMET) Polymerization

ADMET polymerization^{35,36} is a step-condensation polymerization where dienes are connected via metathesis in a stepwise fashion to produce polyenes as depicted in Figure 1-12. Monomer is consumed in the early stages of the reaction to produce dimer, trimer, tetramer, etc with the evolution of the condensate, a small monoene. Each species in the system can react with any other species resulting in a distribution of homologous products. As each step is reversible, the condensate may also react with homologues splitting the chains to smaller species and in a closed system, this reverse reaction restrains the equilibrium product mixture to relatively low molecular weight species. In the typical case involving α,ω -dienes, the ethylene liberated with each connection is easily removed under reduced pressure to drive the equilibrium to the right yielding a product distribution with progressively higher average molecular weight. The equilibrium nature of the reaction permits the reaction of all species in the system, which randomizes the product distribution to the most probable distribution described by the polydispersity index, $PDI = \overline{M}_w / \overline{M}_n = 2.0$.

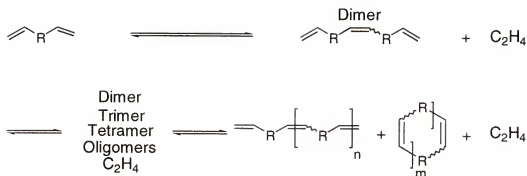


Figure 1-12. The ADMET step/condensation polymerization of an α,ω -diene.

For typical step/condensation polymerizations, the relationship between the number average degree of polymerization (\overline{DP}_n), the conversion (ρ), and the stoichiometric imbalance (r) is described by Equations 1-1. In this relation, r is the molar ratio of groups "A" to groups "B" which condense to form the polymer linkages. In the limit of 100% conversion ($\rho = 1.000$), Equation 1-1a reduces to 1-1b. It can be seen from Equation 1-1b that any decrease in " r " from unity results in a decrease in the maximum obtainable average molecular weight.

$$\overline{DP}_n = \frac{1+r}{1+r-2\rho} \quad \text{Eqn (1-1a)} \qquad \overline{DP}_n = \frac{1+r}{1-r} \quad \text{Eqn (1-1b)}$$

Attainment of high molecular weight requires near perfect stoichiometric balance of the reactive groups³⁷, a concept that must be modified to apply to ADMET. The ADMET polymerizations to date are somewhat unique amongst condensation polymerizations in that the functional groups, which condense to form the linkages in the polymer backbone, are not chemically different. They do not fit into the schemes of A-A + B-B or A-B type polymerizations where different functional groups "A" and "B" react, common examples of which are polyesterifications schematically represented in Figure 1-

13. In the second case in which a hydroxy-functional carboxylic acid condenses to a polyester, $r = 1.000$ due to the fact that both the “A” and “B” groups are in a single monomer. An exception to these polycondensation schemes similar to ADMET is the hydrolytic step-polymerization of dichlorosilanes³⁸ in which Si-Cl groups are converted to silanol groups which then condense with each other to form siloxanes and the condensate, water. Of course in this particular type of polymerization, the SiOH groups may also react with any residual SiCl groups to form the same polymer.

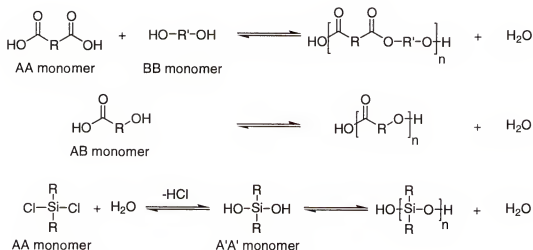


Figure 1-13. Comparison of classical condensation polymerizations.

Therefore, perfect stoichiometric balance in the case of ADMET simply means that vinyl groups terminate all linear molecules in the system at both ends throughout the course of the reaction. In this light, the relationship between \overline{DP}_n and conversion is more appropriately described by Equation 1-2a, often referred to as the Carothers equation, where f_{avg} is the average functionality of all linear species. For perfectly difunctional species, $f_{\text{avg}} = 2.0$, and the more commonly presented Equation 1-2b results.

$$\overline{DP}_n = \frac{2}{2 - \rho f_{avg}} \quad \text{Eqn (1-2a)}$$

$$\overline{DP}_n = \frac{1}{1 - \rho} \quad \text{Eqn (1-2b)}$$

Any loss of vinyl groups due to competing chemistry decreases f_{avg} and lowers the maximum achievable molecular weight. This critical requirement for successful ADMET polymerization deferred its development until the arrival of the well-defined Schrock W(VI) and Mo(VI) carbenes (cf Figure 1-5). Initial attempts to polymerize dienes as early as 1970 were destined to failure as the classical catalyst systems of that time period participated in side reactions which decreased f_{avg} .^{39,40} The reaction was revisited in 1987 by Wagener and coworkers with the realization that the key to success was the utilization of single-site catalysts.⁴¹ The α,ω -dienes 1,5-hexadiene and 1,9-decadiene were condensed to high molecular weight linear polymers utilizing W catalyst **1.1c**.^{35,41} The reaction has since been demonstrated with other Schrock alkylidines, most commonly catalyst **1.2d**, with homogeneous W(VI) classical catalysts⁴² activated by alkyl tin cocatalysts, and most recently with ruthenium catalyst **1.4**.⁴³

Successful demonstration of the ADMET reaction was followed by systematic studies designed to delineate monomer structure reactivity relationships, the bulk of which has centered on Mo catalyst **1.2d**. It became clear that the slower kinetics of the ADMET reaction relative to faster processes such as ROMP and RCM placed greater restraints on the type and placement of functionality in substrates. For dienes with Lewis basic functionalities appropriately placed within the structure, reaction may be prohibitively slow or even completely halted. This effect has been attributed to intramolecular coordination of the Lewis basic functionality, schematically represented in Figure 1-14, and finds precedent in similar ROMP systems.⁴⁴ The degree to which the

ADMET reaction is hindered may depend on the stability and persistence of this chelate. This effect, termed the negative neighboring group effect, has been noted for a variety of functionality but can generally be overcome through monomer design by separating the Lewis basic group "X" from the olefin groups by a suitable number of methylene spacers.

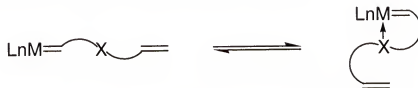


Figure 1-14. The proposed negative neighboring group effect.

With the knowledge of the keys for successful ADMET chemistry in hand, polymers with a broad range of functionality have been prepared including ether, ketone, ester, amine, thioether, conjugated olefins, silane, siloxane, and metal-containing groups.³⁶ Just as for other catalyzed polymerizations, the scope of the ADMET reaction continues to evolve as a result of new developments in catalyst design. Most recently, the arrival of the extremely robust ruthenium catalyst **1.4** has allowed the direct preparation of hydroxy-functional polymers. With the realization of classical systems activated by main-group metals with diminished Lewis acidity, ADMET polymers can now be prepared without the necessity for preformed metal carbenes.^{42,45} A particularly novel twist to this concept was reported where tin-containing dienes were prepared which function both as monomer and as cocatalysts.⁴⁵

Summary of Results Presented in this Dissertation

The ADMET reaction and the polymers produced thereof share many characteristics with other common step/condensation polymerization systems. High molecular weight polymers can only be obtained when the equilibrium between terminal

and internal olefins can be driven to high conversion, a direct consequence of the relation between \overline{DP}_n and conversion described by Equation 1-2b. A further consequence is that the reverse reaction may also be driven in high conversion, where high molecular weight polyalkenamers may be depolymerized to low molecular weight species. The relationship between f_{avg} and \overline{DP}_n (Equation 1-2a) may also be capitalized upon to control molecular weight through the incorporation of monoenes, or chain limiters, in the forward ADMET reaction. End-functionalized oligomers and polymers may be prepared by either the forward or reverse reaction if functionalized chain limiters are employed (Figure 1-15).

Chapter 3 describes results obtained concerning the depolymerization of high molecular weight polybutadiene to prepare low molecular weight species and end-functionalized polymers utilizing complex **1.4**. The unprecedented stability of **1.4** in the presence of ethylene implicated it as a good candidate to catalyze the exact microscopic reverse of the ADMET reaction, whereby polyalkenamers are depolymerized with ethylene as chain limiter. This assumption was born out as much higher conversions in this reaction were achieved than previously possible with well-defined W and Mo alkylidenes. In addition, the unique ability of **1.4** to initiate depolymerization of polybutadiene in the solid state was observed and exploited to prepare end-functionalized polybutadiene.

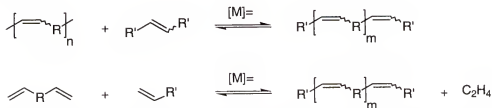


Figure 1-15. ADMET depolymerization and polymerization with chain limiters.

With judicious choice of catalyst system with reactivity appropriate to a given type of diene monomer, linear polymers with highly pure microstructure are obtained. The only variation in structural homogeneity is the olefinic cis/trans ratio, which is typically $\geq 70\%$ trans. This backbone unsaturation provides sites for post-polymerization reaction by which novel polymers may be prepared that are difficult or impossible to obtain by direct means. One such reaction, which has generated both commercial² and high academic interest is hydrogenation whereby the carbon-carbon double bonds are converted to single bonds. It was discovered in our laboratories that addition of silica gel to a completed metathesis reaction catalyzed by ruthenium complex **1.4** followed by exposure to hydrogen gas constitutes an efficient method for catalytic heterogeneous hydrogenation of the metathesis products. The development of this process and its application to the indirect synthesis of saturated polymers, including telechelic polyethylene, are described in Chapter 4.

The highly pure microstructure of ADMET polymers appoints this polymerization route as a means to prepare well-defined models for polymers with less pure constitution. ADMET polymerization coupled with quantitative olefin hydrogenation has been shown⁴⁶⁻⁵¹ to be particularly well suited for the preparation of models for polyethylene and ethylene copolymers as shown in Figure 1-16. Any functionality (R), within the restraints imposed by catalyst compatibility, may be incorporated at regular intervals along a polymer which is in essence a perfectly linear terpolymer of ethylene, butadiene and a monomer containing the functionality. The number of methylene spacers ("n" in Figure 1-16) incorporated in the monomer synthesis precisely controls the frequency of the desired functionality in the polymer backbone. Saturation of the backbone double



CHAPTER 2 EXPERIMENTAL

Instrumentation and Analysis

^1H NMR 300 MHz and ^{13}C NMR 75 MHz were recorded on a Gemini Series NMR Superconducting Spectrometer System or a Varian VXR-300. NMR spectra were recorded in chloroform-*d* (CDCl_3), benzene-*d*₆ (C_6D_6), toluene-*d*₈, and bromobenzene-*d*₅. Resonances are referenced to residual protio solvent and reported in δ units downfield from TMS at 0.0 ppm. Heteronuclear decoupled quantitative ^{13}C NMR spectra were acquired over 8-12 hours with a pulse delay of 20s. Gas chromatographic measurement of purity and product distributions were conducted with a Hewlett-Packard HP5880A gas chromatograph with cross-linked methyl silicone gum capillary column and flame ionization detector. Low and high-resolution mass spectrometry data were recorded on a Finnigan MAT 95Q or Finnigan MAT GCQ Gas Chromatograph/Mass Spectrometer utilizing either electron ionization or chemical ionization. Elemental analyses were conducted by Atlantic Microlab, Inc., Norcross, GA, where each recorded value is the average of duplicate analyses.

Differential Scanning Calorimetric (DSC) and Thermogravimetric Analysis (TGA) data were obtained with a Perkin Elmer 7 Series Thermal Analysis System. DSC samples (5-10mg) were analyzed with either liquid nitrogen or ice as coolant and under a Helium flow rate of 25 ml/min. All samples were pre-dried at 40-50°C under reduced

pressure (<0.1 mm Hg) for 8-12 hours. The instrument was calibrated in the appropriate temperature ranges with cyclohexane and/or ultra-high purity water (subambient measurements), or Indium. Samples were heated to at least 40°C above the melting point to erase thermal history and then scanned at $5^{\circ}\text{C}/\text{min}$, cooling cycle first. TGA samples (5-10 mg) were heated at $20^{\circ}\text{C}/\text{min}$ under N_2 or air with a flow rate of 30 ml/min, until complete combustion.

Gel Permeation Chromatography (GPC) was performed using a Waters Associates Liquid Chromatograph U6K equipped with tandem ABI Spectraflow 757 UV absorbance detector and a Perkin-Elmer LC-25 RI detector. The GPC solvent delivery system was configured for elution with either HPLC grade CDCl_3 or THF through an Ultrastaygel linear mixed bed column (CHCl_3) or through $5 \times 10^3 \text{ \AA}$ and $5 \times 10^4 \text{ \AA}$ Phenogel columns in series (THF). Solvents were sonicated immediately prior to use and delivered at a rate of 1.0 ml/min. Retention times were calibrated against narrow ($\text{PDI} < 1.07$) polystyrene standards (Scientific Polymer Products, Inc) with $M_p = 1900, 7700, 12000, 30000, 59000, 79000, \text{ and } 139400 \text{ g/mol}$. Polymer samples were prepared in HPLC grade THF or CHCl_3 ($\sim 1\%$ w/w) and slowly passed through a 50μ syringe filter prior to injection. Molecular weight measurements by vapor pressure osmometry (VPO) were conducted utilizing a Jupiter Instruments Model 233 with toluene as solvent at 50°C . The instrument constant was determined by calibration ($R^2 > 0.98$) with recrystallized sucrose octaacetate and verified against narrow PDI polystyrene GPC standards (error in measured $M_n \leq 5\%$).

Materials and Techniques

The olefin metathesis catalysts $\text{Ru}(\text{=CHPh})(\text{PR}_3)_2\text{Cl}_2$, R = cyclohexyl or phenyl, and $\text{Mo}[\text{=CHC}(\text{CH}_3)_2\text{Ph}](\text{N-2,6-C}_6\text{H}_3\text{-i-Pr}_2)[\text{OCCH}_3(\text{CF}_3)_2]_2$ were prepared according to published methods. These catalysts were graphically depicted in the appropriate sections of Chapter One. Polybutadiene ($\text{MW} = 2 \times 10^6$, 98% cis-1,4-repeat unit, Aldrich # 18,374-4) was purified by precipitation from methylene chloride into methanol, then degassed and azeotropically dried by dissolution in dry toluene followed by removal of toluene under reduced pressure. It was then stored in an amber bottle inside an argon-purged dry box. Polymer grade ethylene (99.9% min.) was obtained from Matheson and purified by passage through activated molecular sieves followed by two Alltech 8115 High Pressure Oxy-Traps in series. Silica gel-60 (Selecto Scientific cat # 162824, particle size 32-63 μ) used in hydrogenation reactions was sonicated twice in reagent grade CHCl_3 , dried under reduced pressure at 80°C for 24 hours, and stored in an argon-purged dry box until use. 1-Octene, trans-7-tetradecene, 1,9-decadiene, HMPA, diisopropyl amine, bromobenzene, iodomethane, ethyl iodide, and CDCl_3 were dried over CaH_2 and vacuum transferred. Olefin substrates were further degassed by three consecutive freeze/pump/thaw cycles. Pyridine and acetyl chloride were stored over CaH_2 and manipulated under argon. Carbon tetrachloride and methyl formate were distilled under argon from P_2O_5 , with the latter subsequently distilled from CaH_2 . Acetone (reagent grade) was stirred over anhydrous CaSO_4 (100g/L) overnight, decanted to fresh CaSO_4 (50g/L), and distilled immediately prior to use. Acetic anhydride was distilled from anhydrous Na_2CO_3 . Triphenylphosphine (Aldrich, 99%) was dried in the molten state (85°C) with stirring under reduced pressure (5 mm Hg) for 8-12 hours then

stored in an argon purged dry box until use. Diethyl ether and tetrahydrofuran were distilled under argon from Na/K alloy with the respective metal benzophenone ketyls and stored over 5 Å molecular sieves. Toluene was washed with cold conc. H₂SO₄, distilled from Na/K alloy, and stored over 5 Å molecular sieves. All other materials were used as received.

Synthesis and Characterization

ADMET Depolymerizations

Ethenolysis of cis-1,4-Polybutadiene. Depolymerizations were conducted in either glass pressure tubes or glass-lined stainless steel bombs appropriate to the applied pressure. Inside an argon purged dry box polybutadiene **3.1** (500mg, 9.26mmol repeat unit, 400 eq) cut in small chunks and catalyst **1.4** (19 mg, 1 eq) were combined inside the appropriate pressure vessel together with 3 ml CDCl₃. The vessel was sealed, removed to a gas manifold, and opened to a constant dynamic pressure of C₂H₄ with vigorous stirring at room temperature for 48 hours. The reaction vessel was then chilled to avoid loss of volatile products, and the ethylene pressure was slowly vented to the atmosphere. The homogeneous solutions were then immediately exposed to air to decompose any remaining active catalyst. See text for data analysis.

Synthesis of Ester-terminated Polybutadiene(3.5 and 3.6). The chain limiter (**3.4**) was prepared immediately before use by dimerization of ethyl 10-undecenoate (**3.3**). Inside an argon-purged dry box, **3.3** (0.788g, 3.71 mmol, 400 eq) and **1.4** (7.6 mg, 9.25μmol, 1 eq) were combined in a high vacuum flask. The flask was removed to a high vacuum manifold and the contents stirred under reduced pressure at room temperature for

3 hours after which time the reaction was heated to 40°C for an additional 24 hours. Inside the dry box, portions of this dimer/catalyst mixture were combined with polybutadiene 3.1 (500 mg, 9.24 mmol repeat unit) cut in small chunks in glass vials, in two different proportions to generate end-functionalized polymers with predicted DP \approx 20(3.5) and 40(3.6). Stoichiometry: Polymer 3.5 (183 mg dimer 3.4, 46.2 μ mol), Polymer 3.6(91.7 mg dimer 3.4, 23.1 μ mol). Magnetic stir bars were inserted and the vials were sealed and removed from the dry box. The mixtures were occasionally agitated until viscosity was sufficiently reduced that they could be stirred with a magnetic stir plate(12 hours). After stirring for 24 hours, reaction was quenched by placing under reduced pressure then opening to air for 2 hours with stirring. Each polymer was dissolved in toluene and stirred with alumina and filtered to remove catalyst residue, and the toluene was evaporated under reduced pressure to yield clear colorless viscous oils. Yield: 3.5, 592.8 mg, 86.7%; 3.6, 467.3 mg, 78.9%. ^1H - NMR δ (ppm) 3.5 5.39(m, 42H); 4.10(q, 4H); 2.26(t, 4H); 2.03(br, 94H); 1.59(t, 6H); 1.25(br)+1.23(t)=30H. ^{13}C - NMR δ 173.82, 130.27, 130.07, 130.04, 129.95, 129.92, 129.53, 129.37, 60.07, 34.32, 32.65, 32.53, 29.55, 29.26, 29.18, 29.09, 29.03, 27.35, 24.92, 14.21. ^1H - NMR δ (ppm) 3.6 5.39(m, 80H); 4.10(q, 4H); 2.27(t, 4H); 2.03(br, 180H); 1.59(t, 6H); 1.26(br)+1.23(t)=30H.

Metathesis and *in situ* Hydrogenation

Model Study of Hydrogenation using *trans*-7-Tetradecene. Inside an argon-purged dry box, *trans*-7-Tetradecene (1.0 g, 5.09mmol) and **3** (5.2 mg, 0.13 mol%) were combined in a pressure tube containing a magnetic stir bar and stirred 1 hour to allow

complete dissolution of catalyst and alkylidene exchange, during which time the purple heterogeneous mixture became a clear maroon solution. 520 mg silica was added, the tube was immediately sealed, removed to a hydrogen manifold and exposed to a constant 120 psig H₂ at room temperature. Adsorption of the catalyst residue onto the silica surface was indicated by rapid decolorization of the substrate/catalyst solution. After 30 minutes, the reaction was quenched by releasing pressure to the atmosphere and filtration to remove catalyst residue and silica, yielding a clear, colorless liquid. Extent of reduction was estimated by ¹H NMR(CDCl₃) comparing the resonances at 5.4 ppm (multiplet, internal olefin) to that at 0.88 ppm (triplet, CH₃ group). Experiments at each pressure were conducted in triplicate and the average conversions calculated. See text for tabulated results.

Synthesis of 1,18-Bisacetoxyoctadecane (4.2). 9-Decenyl acetate (**4.1**) (1.0g, 5.04mmol) and catalyst **1.4** (5.2 mg, 52μmol) were combined in a high vacuum flask containing a magnetic stir bar. The vessel was sealed, removed to a schlenk line, and opened to a slight positive pressure of argon. It was heated to 60°C with vigorous stirring for 4 hours, after which reaction was continued for an additional 2 hours at ~0.2 mm Hg. The reaction mixture was taken up in 3 ml toluene, combined with 600 mg silica in a pressure tube, and the whole was exposed to 120 psig H₂ at 90°C for 5 hours. Filtration and evaporation of solvent yielded the product as a white powder (0.90 g, 96% yield). LRMS: 372 (m+2). Elemental anal. calcd for C₂₂H₄₂O₄: C, 71.31; H, 11.42. Found: C, 71.37; H, 11.50. ¹H- NMR δ (ppm) 4.02(t, 4H); 2.02(s, 6H); 1.59(m, 4H); 1.23(br, 28H). ¹³C-NMR δ 171.24, 64.65, 29.65, 29.56, 29.52, 29.24, 28.59, 21.02.

Synthesis of Telechelic Polyethylene (4.6). Inside an argon-purged dry box, 1,9-decadiene (3.0g, 21.7mmol, 1 eq), 9-decenyl acetate (4.1) (0.861g, 4.34 mmol, 0.2 eq) and catalyst 1.4 (49mg, 0.06mmol) were combined for a total of 800:1 olefin-to-catalyst ratio. The reaction vessel was sealed, removed to a schlenk line, opened to slight positive pressure of argon and heated to 45°C. Over a period of 6 hours, pressure was slowly decreased (intermittant vacuum) then left open to dynamic vacuum of 10^{-2} mmHg, while slowly increasing temperature to 65°C. After 24 hours, the reaction vessel was sealed and returned to the dry box. 1.5g crude polymer was intimately mixed with 2.5 g silica in a pressure tube, the tube was sealed and removed to a hydrogen manifold. The contents were exposed to 120 psig H₂ at 90°C for 30 minutes. 15 mL toluene was then added via syringe under H₂ purge. The vessel was then exposed to 120 psig H₂ at 90°C with vigorous stirring for 5 hours. Reaction was quenched by release of pressure and filtered while still hot through a heated coarse glass frit to remove catalyst residue and silica. Toluene was removed under reduced pressure to yield 1.45 g white solid. Elemental anal. calcd for [C₁₀₂H₂₀₂O₄]: C, 82.07; H, 13.64. Found: C, 82.03; H, 13.70. ¹H- NMR δ (ppm) (90°C, toluene-d₈) 3.98(t, 4H); 1.73(s, 6H); 1.50(m, 4H); 1.30(br, 220H). $M_n = 1.5 \times 10^3$ (PDI = 1.9, high temp. GPC vs PE), 1.7×10^3 (¹H NMR end-group analysis).

Synthesis of saturated polyester (4.9). Monomer 4.7 was dried by stirring at 50°C for 8-12 hours under reduced pressure (< 0.1 mm Hg) in an appropriate storage flask equipped with a high-vacuum valve. The atmosphere in the flask was deoxygenated by three cycles of evacuation under reduced pressure and replacement with argon, and the monomer was stored under argon. Inside an argon-purged dry box 4.7 (3.00 g, 9.31

mmol, 600 eq) and catalyst **1.4** (12.7 mg, 15.5 μ mol, 1 eq) were combined in a small glass tube with a 24/40 ground glass joint and a magnetic stir bar. The flask was fitted with a Kontes® high vacuum valve, sealed, and attached to a high vacuum sclenk line via ground glass joint sealed with silicone grease. Evolution of ethylene was observed within 5 minutes as evidenced by formation of small bubbles which rapidly increased as the stirrer was set in motion and a 45°C oil bath was raised. The pressure was slowly decreased by applying intermittent vacuum eventually reaching a dynamic vacuum of 10^{-2} - 10^{-3} mm Hg while the temperature was slowly increased to 70°C. After 48 hours, the vessel was sealed and returned to the dry box. Crude yield: 2.70g, 97.8%. A 1.00g chunk of the crude polymer/catalyst residue mixture was combined with 500 mg silica gel in a glass pressure tube containing a magnetic stir bar. 10 mL dry degassed toluene was added and the tube was rapidly sealed with a brass valve fitted via a threaded Teflon™ flange, removed to a gas manifold where it was charged with H₂ (120 psig, dynamic pressure) and heated to 90°C with vigorous stirring. Note: Hydrogen pressure is applied prior to dissolution of the polymer chunk. After 24 hours, pressure was released to the atmosphere and the heterogeneous mixture was filtered while still hot through a coarse glass frit. The reddish-brown silica was washed with hot toluene and the washings were combined with the clear, colorless filtrate. The polymer precipitated on cooling to below 60°C. The toluene was evaporated under reduced pressure to yield **4.9** as a white solid. Yield: 0.96g, 95% based on 1g **4.8**. Elem. Anal. Calcd. for [C₁₉H₃₆O₂]: C, 76.97; H, 12.24. Found: C, 77.06; H, 12.22. . ¹H- NMR δ (ppm) (90°C toluene-d₈) 4.02(t, 2H); 2.17(t, 2H); 1.56(m, 4H); 1.28(br, 28H). ¹³C-NMR δ 177.01, 139.12, 114.06,

51.21, 45.67, 33.76, 32.47, 29.49, 29.35, 29.05, 28.86, 27.42. $M_n = 1.02 \times 10^4$ (PDI = 2.3, high temp. GPC vs PE).

Synthesis of Functionalized Diene Monomers for Model Ethylene Copolymers

Synthesis of extended chain ω -alkenyl bromides and carboxylic acids

Synthesis of 9-decenyl bromide(5.1). 9-Decenol (10g, 64 mmol, 1 eq) and CBr_4 (25.47 g, 76.8 mmol, 1.2 eq) were dissolved in 100 ml anhydrous ether in an argon-filled schlenk flask. A small amount of freshly ground CaH_2 was added and stirred for one hour. Solid PPh_3 (20.14 g, 76.8 mmol, 1.2 eq) was added under argon in ~4 g increments over 20 minutes. After 20 hours the reaction mixture was diluted with 50 mL pentane, filtered, and concentrated under reduced pressure. 11.2 g (80% yield) pure **5.1** (100% GC) was obtained after distillation from CaH_2 (bp = 96-98°C/10 mmHg). ^1H -NMR δ (ppm) 5.78(m, 1H); 4.94(m, 2H); 3.38(t, 2H); 2.02(q, 2H); 1.83(m, 2H); 1.37(m)+1.28(br) = 10H. ^{13}C -NMR δ 139.06, 114.14, 33.95, 33.73, 32.78, 29.24, 28.97, 28.83, 28.68, 28.12.

Synthesis of 10-undecenyl bromide(5.2). The alkenyl bromide was prepared in two steps from the respective alcohol via the tosylate. 10-Undecenol (82.5g, 0.484 mol, 1 eq) was dissolved in 500 mL CHCl_3 in a 1 L schlenk flask. The solution was placed under argon and chilled to 0°C. Pyridine (78 mL, 2 eq) was decanted into the flask from CaH_2 . Solid TsCl (138.4 g, 0.726 mol, 1.5 eq) was added under argon in increments over ~ 1.5 hours. After 8 hours the reaction mixture was washed with water, sat'd NaHCO_3 , 3N HCl, and brine. The organic layer was dried with Na_2SO_4 and concentrated to 154.7

g pale yellow oil which was converted to the bromide without further purification. The crude tosylate was dissolved in 900 mL dry acetone under argon. LiBr_{anh} (126 g, 3 eq) was added in one portion, the flask was fitted with a water-cooled condenser and the mixture was refluxed for 12 hours. The mixture was filtered, diluted with 300 mL pentane, filtered a second time and concentrated. The crude product was taken up in 300 mL pentane and washed with water, sat'd NaHCO₃, and brine. The organic layer was dried with Na₂SO₄, concentrated, and the bromide (97% GC) was vacuum transferred from CaH₂. Yield: 100.8 g, 89 % for two steps. ¹H- NMR δ (ppm) 5.80(m, 1H); 4.95(m, 2H); 3.40(t, 2H); 2.04(q, 2H); 1.85(m, 2H); 1.38(m)+1.29(br) = 12H. ¹³C-NMR δ 139.12, 114.12, 33.96, 33.76, 32.81, 29.33, 29.04, 28.88, 28.71, 28.13.

Synthesis of 11-dodecenoic acid(5.3). 10-Undecenyl bromide (5.2) (10 g, 42.9 mmol, 1.0 eq) was added slowly via syringe to freshly scoured Mg turnings (1.053 g, 43.3 mmol, 1.01 eq) in 50 mL dry THF with rapid stirring under argon. After stirring 2 hours at 45°C, the resulting Grignard solution was rapidly poured into a large beaker containing 19g (~10 eq) finely crushed CO₂ (s). The mixture was stirred with 50 mL 3N HCl and 80 mL pentane, after which the aqueous layer was discarded. The organic layer was washed with 3N HCl and water, dried over Na₂SO₄, and concentrated to 8.16g pale yellow oil. The oil was further purified by distillation under reduced pressure (bp = 110-115°C/0<P<0.1 mmHg) to yield 6.71g colorless oil (79% yield). ¹H-NMR δ (ppm) 11.76(br, 1H); 5.80(m, 1H); 4.93(m, 2H); 2.32(t, 2H); 2.01(q, 2H); 1.60(m, 2H); 1.26(br, 12H). ¹³C-NMR δ 180.62, 139.13, 114.09, 34.11, 33.78, 29.67, 29.38, 29.35, 29.20, 29.07, 29.01, 28.89, 24.63.

Synthesis of 13-tetradecenoic acid(5.5). 10-Undecenyl bromide (5.2) (22.25 g, 95.4 mmol, 1.0 eq) was added slowly via syringe to freshly scoured Mg turnings (2.34 g, 96.2 mmol, 1.01 eq) in 100 mL dry THF with rapid stirring under argon. After stirring 2 hours at 45°C, the resulting Grignard solution was cooled to RT and transferred via cannula to LiCl_(anh) (0.161 g, 1.6 mmol) in 100 ml dry THF at 0°C. β -Propiolactone (Acros, unopened bottle) (5 mL, 79.5 mmol, 0.83 eq) was added dropwise via syringe maintaining the temperature below 5°C. After one hour, reaction was quenched with 50 mL 3N HCl and then concentrated. The crude product was taken up in 200 ml pentane and washed with 3N HCl, water, and brine. The organic layer was dried over Na₂SO₄ and concentrated to 20.03g (over theory) pale yellow oil, which solidified on standing. The product can be further purified by distillation under reduced pressure (bp \equiv 126°C/0<P<0.1 mmHg) or by flash chromatography (20%EtOAc/Pentane) rendering 85 and 91% isolated yields, respectively of a white waxy solid. ¹H- NMR δ (ppm) 11.22(br, 1H); 5.79(m, 1H); 4.92(m, 2H); 2.32(t, 2H); 2.02(q, 2H); 1.61(m, 2H); 1.24(br, 16H). ¹³C-NMR δ 180.64, 139.19, 114.07, 34.12, 33.80, 29.55, 29.47, 29.41, 29.22, 29.13, 29.03, 28.93, 24.64.

Synthesis of 11-dodecenyl bromide(5.4). Following the LAH reduction of 11-dodecenoic acid (5.3) to the respective alcohol, 5.4 was obtained in two steps via the tosylate as described previously for preparation of 5.2. Solid LAH pellets (7.34 g, 1.5 eq) were added in increments over 1 hour to 5.3 (25.6g, 0.129 mol) in 300 mL anhydrous ether under argon and stirred for 8 hours. The solution was chilled below 0°C, quenched with 300 mL 3N HCl, then combined with 100 ml ether. The organic layer was washed

with 3N HCl, water, 1N NaOH, and brine, then dried over Na₂SO₄ and concentrated to 22.8g clear colorless liquid (>99% GC). The resulting 11-dodecenol was converted to the tosylate as described previously. The crude tosylate was recrystallized from MeOH/H₂O, taken up in HCCl₃ and dried with Na₂SO₄, and finally concentrated to 38.19g white solid. The tosylate was converted to **5.4** by the action LiBr in refluxing acetone as described previously, and purified by fractional distillation. Yield: 22.5g, 71% overall for 3 steps. ¹H- NMR δ (ppm) 5.78(m, 1H); 4.93(m, 2H); 3.36(t, 2H); 2.01(q, 2H); 1.83(m, 2H); 1.35(m)+1.28(br) = 14H. ¹³C-NMR δ 139.06, 114.15, 33.96, 33.73, 32.79, 29.30, 29.02, 28.80, 28.67, 28.10.

Synthesis of 13-tetradecenyl bromide(5.6). Prepared from 13-tetradecenoic acid (**5.5**) in three steps as previously described for the preparation of **5.4**, excluding recrystallization of the intermediate tosylate. The bromide was purified by flash chromatography (pentane). Yield: 56 % overall for 3 steps. ¹H- NMR δ (ppm) 5.78(m, 1H); 4.94(m, 2H); 3.38(t, 2H); 2.02(q, 2H); 1.83(m, 2H); 1.36(m)+1.25(br) = 18H. ¹³C-NMR δ 139.16, 114.06, 33.93, 33.81, 32.82, 29.53, 29.42, 29.13, 28.92, 28.77, 28.16.

Synthesis of symmetrical alcohol-functionalized dienes

Synthesis of 11-oxo-1,20-heneicosadiene (5.7). The ketone diene **5.7** was prepared in two steps via Claisen condensation of ethyl 10-undecenoate to form the β-keto ester diene, followed by dealkoxycarbonylation without isolation of the first step. Claisen condensation: Ethyl 10-undecenoate (60mL, 52.44 g, 247 mmol, 1 eq) was added dropwise to a stirring suspension of KH [34.97g (35%wt/wt in mineral oil), 296.4 mmol, 1.2 eq] in 300 ml dry THF at room temperature. After 12 hours, the reaction was

cooled to 0°C, quenched by addition of 30 ml acetic acid, and the solution was poured into 1 L cold D.I. water. The layers were separated and the aqueous phase was extracted with ether (2 x 100 ml). The combined organic solutions were washed with D.I. water (3 x 1L), dried over MgSO₄, and concentrated under reduced pressure to a yellow oil. Crude yield can not be determined as it contains mineral oil from the KH dispersion. Dealkoxycarbonylation: The crude oil was combined with 93.4 g LiCl, 450 ml DMSO, and 20 ml D.I. water and the mixture was sparged with argon for 30 minutes. The mixture was then vigorously stirred at 155°C under argon for 12 hours. Upon cooling to room temperature, the mixture separated and the upper phase solidified. The solid was taken up in 500 ml ether and washed with D.I. water (3 x 300 ml). The resulting crude product was reduced with LAH without further purification. An analytical sample was obtained by recrystallization from methanol. %. ¹H-NMR δ (ppm) 5.78(m, 2H); 4.92(m, 4H); 2.35(tr, 4H); 2.01(q, 4H); 1.53(m, 4H); 1.32(br, 24). ¹³C-NMR δ 211.59, 139.13, 114.11, 42.78, 33.75, 29.33, 29.27, 29.05, 28.88, 23.87.

Synthesis of 11-hydroxy-1,20-heneicosadiene (5.8). Prepared by LAH reduction of crude ketone diene 5.7. The crude ketone was dissolved in 300 ml dry THF under argon in a 500 ml schlenck flask equipped with an addition funnel. LAH (62 mL 1M in THF, 0.5 eq) was added dropwise via the addition funnel at room temperature with stirring. After 12 hours, the solution was cooled to 0°C and quenched by slow addition of 100 ml 3M HCl. Transferred to separatory funnel with 300 ml ether and discarded the aqueous phase. The ether solution was washed with sat'd NaHCO₃ (300 ml), D.I. water (3 x 300 ml), dried over MgSO₄, and concentrated to an oily off-white solid. The pure diene 5.8 was obtained as a white solid after flash chromatography (10%

EtOAc/hexanes). Yield 27.0 g, 70.7% overall for three steps. ^1H - NMR δ (ppm) 5.78(m, 2H); 4.94(m, 4H); 3.55(b, 1H); 2.01(q, 4H); 1.37(m)+1.25(br) = 28H. ^{13}C -NMR δ 139.16, 114.07, 71.94, 37.45, 33.77, 29.66, 29.54, 29.42, 29.10, 28.89, 25.63.

Synthesis of 1,22-tricosadiene-12-ol (5.9). 10-Undecenyl Bromide (**5.2**) (5 g, 21.4 mmol, 1.0 eq) was added slowly via syringe to freshly scoured Mg turnings (0.525 g, 21.6 mmol, 1.01 eq) in 50 mL dry THF with rapid stirring under argon. After stirring 1 hour at 45°C, the resulting Grignard solution was chilled to 0°C and methyl formate (0.63 mL, 0.48 eq) was added dropwise, while maintaining the temperature below 5°C. The contents were warmed to RT, stirred 30 minutes and then concentrated. The product mixture was taken up in pentane and 3N HCl. The organic layer was washed with 3N HCl and water, dried over Na_2SO_4 , and concentrated to 3.0 g white solid. The alcohol was purified by flash chromatography (10%EtOAc/Hexanes). Yield: 2.76g, 76.6%. ^1H -NMR δ (ppm) 5.78(m, 2H); 4.92(m, 4H); 3.55(b, 1H); 2.01(q, 4H); 1.37(m)+1.25(br) = 32H. ^{13}C -NMR δ 139.16, 114.06, 71.94, 37.47, 33.77, 29.69, 29.59, 29.53, 29.46, 29.11, 28.91, 25.63.

Synthesis of 1,24-pentacosadiene-13-ol (5.10). Diene **5.10** was prepared by reaction of 11-dodecenyl magnesium bromide (from **5.4**) with methyl formate utilizing similar protocol described previously for preparation of diene **5.9**. Yield: 81.4%. NMR spectra identical within experimental error with that of **5.9**.

Synthesis of 1,28-nonacosadiene-15-ol (5.11). Diene **5.11** was prepared by reaction of 13-tetradecenyl magnesium bromide (from **5.6**) with methyl formate utilizing

similar protocol described previously for preparation of diene 5.9. Yield: 39 %. NMR spectra identical within experimental error with that of 5.9.

Synthesis of symmetrical dienes with pendant acetate groups

General procedure for acetylating alcohol-functional dienes. The alcohol diene was weighed into a schlenk flask and dried by either stirring in the molten state at 45-70°C under reduced pressure (< 5 mmHg) for several hours or by dissolution in dry toluene followed by evaporation under reduced pressure. Excess AcCl (4-10 eq) was added dropwise to a solution of the alcohol in either dry toluene or anhydrous ether containing pyridine (slight excess over that of AcCl). Both AcCl and pyridine were transferred via syringe after storage over CaH₂ under argon. After aqueous workup, the crude acetates were purified by flash chromatography (2-3%EtOAc/pentane or hexanes). Products obtained in this manner were free of detectable impurities (GC, NMR) with the exception of 15-acetoxy-1,28-nonacosadiene which required further purification by HPLC (normal phase, 2%EtOAc/hexanes) to separate impurities with nearly identical R_f values, possibly caused by side reaction (see below).

Synthesis of 11-acetoxy-1,20-heneicosadiene (5.12). Prepared as described above from 5.8. Yield: 82%, clear, colorless oil (100% GC). LRMS: 351 (m+). Elem. Anal. Calcd. for C₂₃H₄₂O₂: C, 78.80; H, 12.08. Found: C, 78.82; H, 12.21. ¹H-NMR δ (ppm) 5.77(m, 2H); 4.94(m)+4.83(p) = 5H; 2.02(q)+1.99(s) = 7H; 1.46(m, 4H); 1.34(m)+1.23(br) = 24H. ¹³C-NMR δ 170.71, 139.02, 114.04, 74.27, 34.05, 33.73, 29.41, 29.33, 29.03, 28.85, 25.24, 21.15.

Synthesis of 12-acetoxy-1,22-tricosadiene (5.13). Prepared as described above from 5.9. Yield: 86%, clear, colorless oil (100% GC). LRMS: 378 (m+). Elem. Anal. Calcd. for $C_{25}H_{46}O_2$: C, 79.30; H, 12.25. Found: C, 79.25; H, 12.29. 1H -NMR δ (ppm) 5.77(m, 2H); 4.94(m)+4.83(p) = 5H; 2.02(q)+1.99(s) = 7H; 1.46(m, 4H); 1.34(m)+1.23(br) = 28H. ^{13}C -NMR δ 170.82, 139.13, 114.06, 74.36, 34.10, 33.76, 29.47, 29.42, 29.09, 28.91, 25.28, 21.23.

Synthesis of 13-acetoxy-1,24-pentacosadiene (5.14). Prepared as described above from 5.10. Yield: 93%, clear, colorless oil (100% GC). LRMS: 406 (m+). Elem. Anal. Calcd. for $C_{27}H_{50}O_2$: C, 79.74; H, 12.39. Found: C, 79.81; H, 12.45. 1H -NMR δ (ppm) 5.77(m, 2H); 4.94(m)+4.83(p) = 5H; 2.02(q)+1.99(s) = 7H; 1.46(m, 4H); 1.34(m)+1.23(br) = 32H. ^{13}C -NMR δ 170.86, 139.10, 114.07, 74.36, 34.15, 33.70, 29.49, 29.43, 29.03, 28.85, 25.24, 21.17.

Synthesis of 15-acetoxy-1,28-nonacosadiene (5.15). Prepared as described above from 5.11. Violent reaction occurred upon addition of AcCl (evolution of gas, exotherm, and formation of black particulates) perhaps due to adventitious moisture. Yield: 62 %, white solid (100% GC). LRMS: 463 (m+1). Elem. Anal. Calcd. for $C_{31}H_{58}O_2$: C, 80.45; H, 12.63. Found: C, 80.39; H, 12.75. 1H -NMR δ (ppm) 5.78(m, 2H); 4.93(m)+4.80(p) = 5H; 2.02(q)+2.00(s) = 7H; 1.47(m, 4H); 1.33(m)+1.23(br) = 40H. ^{13}C -NMR δ 170.89, 139.21, 114.06, 74.41, 34.10, 33.81, 29.62, 29.60, 29.56, 29.53, 29.50, 29.14, 28.93, 25.30, 21.28.

Synthesis of symmetrical dienes with pendant carboxylic acid and alkoxycarbonyl groups

Synthesis of 2-(9-decenyl)-11-dodecenoic acid(5.18). Diene **5.18** was prepared by C-alkylation of the dianion (enolate) of 11-dodecenoic acid (**5.3**) with 9-decenyl bromide (**5.1**). The dianion of **5.3** was generated by reaction with 2 eq LDA prepared *in situ*. All manipulations were conducted using standard schlenk techniques under argon atmosphere. Butyl lithium (74.4 mL 2.5M in hexanes, 0.186 mol, 2.05 eq) was added slowly via syringe to diisopropyl amine (26.2 mL, 0.186 mol, 2.05 eq) in 100 mL THF while maintaining the temperature at $-15^{\circ}\text{C} \geq T \geq -30^{\circ}\text{C}$. The solution was stirred 5 min at -20°C , then 15 minutes at RT. **5.3** (18 g, 90.8 mmol, 1.0 eq) was added slowly via syringe while maintaining the temperature at $-15^{\circ}\text{C} \geq T \geq -30^{\circ}\text{C}$ during which a milky white suspension formed. The solution was cooled to 0°C and HMPA (15.8 mL, 90.8 mmol, 1.0 eq) was added via syringe followed by rapid addition of **5.1** (19.9 g, 90.8 mmol, 1.0 eq) via syringe at which time the solution temperature elevated to $15-20^{\circ}\text{C}$. After stirring 12 hours the reaction was chilled to 0°C , quenched with 500 mL ice cold 3N HCl, and concentrated under reduced pressure. The heterogeneous aqueous mixture was extracted with pentane and the organic layer washed with 3N HCl, water and brine, then dried over Na_2SO_4 and concentrated to ~38g pale yellow oil. The oil was further purified by flash chromatography (15%EtOAc/pentane) to render pure **5.18** in 71% isolated yield as a white solid. ^1H -NMR δ (ppm) 5.7(m, 2H); 4.94(m, 4H); 2.33(m, 1H); 2.01(q, 4H); 1.63(m, 2H); 1.48(m)+1.27(br) = 26H. ^{13}C -NMR δ 183.26, 139.15, 114.11, 45.57, 33.79, 32.12, 29.51, 29.39, 29.09, 28.89, 27.34.

Synthesis of 2-(11-dodecenyl)-13-tetradecenoic acid(5.19). Diene 5.19 was prepared by C-alkylation of the dianion (enolate) of 13-tetradecenoic acid (5.5) with 11-dodecenyl bromide (5.4), following the same procedures for preparation and purification described previously for diene 5.18. The carboxylic acid was isolated as a white powder in 82% yield. ^1H -NMR δ (ppm) 5.7(m, 2H); 4.94(m, 4H); 2.33(m, 1H); 2.01(q, 4H); 1.63(m, 2H); 1.48(m)+1.27(br) = 34H. ^{13}C -NMR δ 183.34, 139.10, 114.105, 45.63, 33.82, 32.11, 29.49, 29.38, 29.11, 28.80, 27.32.

Synthesis of 2-(8-nonenyl)-12-tridecenoic acid(5.25). Diene 5.25 was prepared by C-alkylation of the dianion (enolate) of 10-undecenoic acid (Acros) with 10-undecenyl bromide (5.2), following the same procedures for preparation and purification described previously for diene 5.18. The carboxylic acid was isolated as a clear, colorless oil in 85% yield.

Synthesis of methyl 2-(11-dodecenyl)-13-tetradecenoate (5.22). Diene 5.22 was prepared by base-catalyzed O-alkylation of carboxylic acid diene 5.19 with MeI. Anhydrous K_2CO_3 (1.32 g, 9.6 mmol, 2.5 eq) and 5.19 (1.5 g, 3.8 mmol, 1 eq) were combined with 50 mL dry acetone in a schlenk flask fitted with a water-cooled condenser under argon. MeI (1.9 mL, 30.5 mmol, 8 eq) was added via syringe. The mixture was heated with a 60-70°C oil bath for 24 hours with vigorous stirring. To minimize loss of MeI due to evaporation, the condenser temperature was maintained at 15°C and the argon backpressure was slightly increased over atmospheric. Two additional aliquots of MeI (2 mL) were added at intervals via syringe. The acetone was evaporated under reduced pressure and the concentrate was taken up in 50 mL pentane and water. The organic

layer was washed with sat'd NaHCO_3 , 3N HCl, and brine, dried over Na_2SO_4 and concentrated to 1.57g pale yellow oil. The oil was further purified by flash chromatography (5%EtOAc/hexanes) to 1.45g (93.5%) **5.22** as a clear colorless oil (100% GC). LRMS(EI): 406 (m+). Elem. Anal. Calcd. for $\text{C}_{27}\text{H}_{50}\text{O}_2$: C, 79.74; H, 12.39. Found: C, 79.79; H, 12.54. ^1H - NMR δ (ppm) 5.80(m, 2H); 4.94(m, 4H); 3.70(s, 3H) 2.35(m, 1H); 2.04(q, 4H); 1.61(m, 2H); 1.39(m)+1.23(br) = 34H. ^{13}C -NMR δ 177.06, 139.18, 114.06, 51.24, 45.70, 33.80, 32.49, 29.54, 29.46, 29.13, 28.91, 27.46.

Synthesis of methyl 2-(9-Decenyl)-11-dodecenoate (5.20). Diene **5.20** was prepared by base-catalyzed O-alkylation of carboxylic acid diene **5.18** with MeI, utilizing similar procedures for synthesis and isolation described previously for **5.22** (100% GC). Yield: 88%. LRMS(EI): 351 (m+). Elem. Anal. Calcd. for $\text{C}_{23}\text{H}_{42}\text{O}_2$: C, 78.80; H, 12.08. Found: C, 78.90; H, 12.26. ^1H - NMR δ (ppm) 5.77(m, 2H); 4.92(m, 4H); 3.63(s, 3H) 2.29(m, 1H); 2.00(q, 4H); 1.55(m, 2H); 1.33(m)+1.23(br) = 26H. ^{13}C -NMR δ 177.01, 139.12, 114.06, 51.21, 45.67, 33.76, 32.47, 29.49, 29.35, 29.05, 28.86, 27.42.

Synthesis of ethyl 2-(9-Decenyl)-11-dodecenoate (5.21). Diene **5.21** was prepared by base-catalyzed O-alkylation of carboxylic acid diene **5.18** with EtI, utilizing similar procedures for synthesis and isolation described previously for **5.22** (100% GC). Yield: 83%. LRMS(EI): 365 (m+). Elem. Anal. Calcd. for $\text{C}_{24}\text{H}_{44}\text{O}_2$: C, 79.06; H, 12.16. Found: C, 79.10; H, 12.26. ^1H - NMR δ (ppm) 5.77(m, 2H); 4.92(m, 4H); 4.13(q, 2H) 2.34(m, 1H); 2.04(q, 4H); 1.55(m, 2H); 1.33(m)+1.23(br) = 29H. ^{13}C -NMR δ 176.51, 139.13, 114.06, 59.85, 45.72, 33.76, 32.47, 29.50, 29.36, 29.06, 28.89, 27.39, 14.32.

Synthesis of 2-(methyl)-11-dodecenoic acid(5.25). **5.25** was prepared by C-alkylation of the dianion (enolate) of propionic acid with 9-decenyl bromide (**5.1**), following the same procedures for preparation and purification described previously for diene **5.18**. The carboxylic acid was isolated as a clear colorless oil in 70.8% yield. ^1H -NMR δ (ppm) 11.34(br, 1H); 5.78(m, 1H); 4.94(m, 2H); 2.43(m, 1H); 2.01(q, 2H); 1.62(m, 1H); 1.32(m)+1.27(br)+1.15(d,) = 16H. ^{13}C -NMR δ 183.69, 139.16, 114.09, 39.39, 33.78, 33.49, 29.45, 29.39, 29.07, 28.89, 27.10, 16.80.

Synthesis of 2-(9-decenyl)-2-methyl-11-dodecenoic acid(5.23). **5.23** was prepared by C-alkylation of the dianion (enolate) of 2-(methyl)-11-dodecenoic acid (**5.25**) with 9-decenyl bromide (**5.1**), following the same procedures for preparation and purification described previously for diene **5.18**. The carboxylic acid was isolated as a clear colorless oil in 76 % yield. ^1H - NMR δ (ppm) 5.78(m, 2H); 4.93(m, 4H); 2.01(q, 4H); 1.59(m, 2H); 1.35(m)+1.25(br)+1.11(s) = 33H. ^{13}C -NMR δ 184.73, 139.16, 114.11, 45.75, 39.06, 33.80, 30.12, 29.43, 29.11, 28.91, 24.43, 20.99.

Synthesis of methyl 2-(9-decenyl)-2-methyl-11-dodecenoic acid (5.24). Diene **5.24** was prepared by base-catalyzed O-alkylation of carboxylic acid diene **5.23** with MeI, utilizing similar procedures for synthesis and isolation described previously for **5.22** (100% GC). Yield: 96%. LRMS(EI): 364 (m+). ^1H - NMR δ (ppm) 5.77(m, 2H); 4.92(m, 4H); 3.61(s, 3H); 2.00(q, 4H); 1.55(m, 2H); 1.34(m)+1.22(br) = 26H; 1.07(s, 3H). ^{13}C -NMR δ 178.09, 139.12, 114.07, 51.38, 45.92, 39.44, 33.77, 30.07, 29.40, 29.08, 28.88, 24.51, 21.13.

Synthesis of symmetrical dienes with pendant chloride and phenyl groups

Synthesis of 11-chloro-1,20-heneicosadiene (5.16). **5.8** (2.0 g, 65 mmol, 1 eq) in 10 mL CCl_4 was added via cannula under argon to Ph_3P (5.5 g, 21 mmol, 3.2 eq) in 20 mL CCl_4 . The vessel was heated in an 80°C oil bath for 16 hours, during which time a white precipitate formed and the solution developed a yellow tinge. The mixture was filtered and the solids washed with pentane. Addition of the pentane washings to the filtrate caused additional precipitation, which was again filtered, and the resulting liquid was concentrated under reduced pressure. Repeated dissolution in minimal pentane, chilling, and filtration followed by concentration yielded 2.17g slightly cloudy liquid. Pure (100% GC) diene **5.16** was obtained after flash chromatography (pentane) as a clear, colorless liquid. **Note:** Ph_3P and **5.8** were dried in the molten state under reduced pressure prior to use and CCl_4 was distilled from P_2O_5 (A previous attempt with less rigorous exclusion of moisture gave much lower yields). Yield: 1.8g, 85%. LRMS(EI): 326 (m+). Elem. Anal. Calcd. for $\text{C}_{21}\text{H}_{39}\text{Cl}$: C, 77.14; H, 12.02. Found: C, 77.07; H, 12.13. ^1H -NMR δ (ppm) 5.79(m, 2H); 4.94(m, 4H); 3.86(m, 1H); 2.02(q, 4H); 1.69(m, 4H); 1.50(m)+1.36(m)+1.27(br) = 24H. ^{13}C -NMR δ 139.13, 114.12, 64.29, 38.50, 33.80, 29.45, 29.40, 29.16, 29.09, 28.90, 26.48.

Synthesis of 11-phenyl-1,20-heneicosadiene (5.17). Diene **5.17** was prepared via nucleophilic attack of phenyl lithium on ketone diene **5.7**, followed by *in situ* deoxygenation of the resulting tertiary benzylic alkoxide. Bromobenzene (2.0 mL, 19.6 mmol, 2 eq) in 20 mL ether was added slowly to lithium foil (1.087g, 157 mmol, 16eq) in 40 mL ether under argon. After refluxing for 1 hour, ketone diene **5.7** (3g, 9.79 mmol, 1

eq) in 20 mL ether was added slowly and the mixture was stirred for 1 hour. The mixture was chilled to -50°C and ~ 50 mL NH_3 was condensed into the flask from a tank at which time the reaction turned blue. After 10 minutes, the reaction was quenched via addition of 11 g $\text{NH}_4\text{Cl}(\text{anh})$ in portions through a solids addition funnel. The ammonia was evaporated, the mixture was filtered and the ether solution was washed with brine and D.I. water. Pure (100% GC) diene **5.17** was obtained after flash chromatography (pentane) as a clear, colorless liquid. 2.2 g, 61 % yield. LRMS(EI): 368 (m+). Elem. Anal. Calcd. for $\text{C}_{27}\text{H}_{44}$: C, 87.97; H, 12.03. Found: C, 88.00; H, 12.06. ^1H -NMR δ (ppm) 7.25(m, 2H); 7.20(m, 3H); 5.79(m, 2H); 4.95(m, 4H); 2.45(m, 1H); 2.01(q, 4H); 1.54(m, 4H); 1.34(m)+1.21(br) = 24H. ^{13}C -NMR δ 146.37, 139.18, 128.10, 127.63, 125.66, 114.06, 46.06, 36.97, 33.79, 29.73, 29.47, 29.10, 28.91, 27.60.

Synthesis of ADMET Model Ethylene/Polar Monomer Copolymers

General Procedure for Preparation of Model Polymers. The pure diene monomers may be adequately dried and degassed by replacing the atmosphere three times with argon via three successive pump/purge cycles and then stirring under reduced pressure at 50°C for several hours. The ADMET polymerizations and subsequent hydrogenations were all conducted utilizing the procedure described for polymers **4.6** and **4.9**. Inside an argon-purged dry box, monomer and catalyst (400:1) were combined in a small tube with a single 24/40 neck and containing a magnetic stir bar. The tube was sealed with a Kontes high vacuum valve, removed to a vacuum line and the pressure was reduced in steps ultimately reaching $10^{-2} - 10^{-3}$ mm Hg while increasing the temperature to 65°C . Alternately, the reaction may be conducted in a pressure tube fitted with a vacuum valve

via teflon bushing thereby eliminating the need to transfer the ADMET polymer to another vessel before hydrogenation. A homemade magnetic stirrer constructed from a powerful magnet and a stir motor was utilized to maintain agitation as long as possible as the viscosity increased during the polymerization. After 48 hours, the vessel was sealed and returned to the dry box. In a glass pressure tube, the polymer/catalyst mixture was combined with silica gel-60 (100 X the weight of catalyst) and sufficient toluene to aid dispersion (generally 10-15 ml for 500 mg polymer). Hydrogen pressure was applied as quickly as possible, within 2-3 minutes, to deactivate the catalyst residue toward metathesis prior to dissolution of the polymer. The mixture was then heated to 90°C with vigorous stirring while maintaining a constant pressure of 120 psig H₂ for 24 hours. The mixture was filtered to remove the silica/catalyst residue composite and the toluene evaporated to yield colorless viscous or water-white solid polymers. Number average molecular weights for these polymers as measured by GPC(vs polystyrene) were consistently in the range $2 - 5 \times 10^4$ g/mol (PDI \cong 2.0).

Synthesis of ADMET model ethylene/vinyl acetate copolymers

ADMET/Hydrogenation of 11-acetoxy-1,20-heneicosadiene (HP5.12). Elem.

Anal. Calcd. for [C₂₁H₄₀O₂]: C, 77.72; H, 12.42. Found: C, 77.63; H, 12.50. ¹H-NMR δ (ppm) 4.83(p, 1H); 2.02(s, 3H); 1.50(br, 4H); 1.23(br, 32H). ¹³C-NMR δ 170.86, 74.45, 34.15, 29.71, 29.58, 25.33, 21.28.

ADMET/Hydrogenation of 12-acetoxy-1,22-tricosadiene (HP5.13). Elem. Anal.

Calcd. for [C₂₃H₄₄O₂]: C, 78.35; H, 12.58. Found: C, 78.16; H, 12.63. ¹H-NMR δ (ppm)

4.82(p, 1H); 2.03(s, 3H); 1.49(br)+1.25(br) = 40H. ^{13}C -NMR δ 170.88, 74.42, 34.13, 29.65, 29.53, 29.29, 29.17, 25.31, 21.26.

ADMET/Hydrogenation of 13-acetoxy-1,24-pentacosadiene (HP5.14). Elem.

Anal. Calcd. for $[\text{C}_{25}\text{H}_{48}\text{O}_2]$: C, 78.88; H, 12.71. Found: C, 78.83; H, 12.76. ^1H -NMR δ (ppm) 4.83(p, 1H); 2.01(s, 3H); 1.47(br)+1.22(br) = 44H. ^{13}C -NMR δ 170.93, 74.44, 34.11, 29.70, 29.58, 29.54, 25.31, 21.23.

ADMET/Hydrogenation of 15-acetoxy-1,28-nonacosadiene (HP5.15). Elem.

Anal. Calcd. for $[\text{C}_{29}\text{H}_{56}\text{O}_2]$: C, 79.75; H, 12.92. Found: C, 79.61; H, 12.94. ^1H -NMR δ (ppm) 4.83(p, 1H); 2.01(s, 3H); 1.47(br, 4H); 1.22(br, 48H). ^{13}C -NMR δ 170.80, 74.38, 34.10, 29.62, 29.564, 29.50, 29.09, 25.30, 21.29.

Synthesis of ADMET model ethylene/acrylate model copolymers

ADMET/Hydrogenation of methyl 2-(11-dodecenyl)-13-tetradecenoate (HP5.22).

Elem. Anal. Calcd. for $[\text{C}_{25}\text{H}_{48}\text{O}_2]$: C, 78.88; H, 12.71. Found: C, 78.92; H, 12.78. ^1H -NMR δ (ppm) 3.71(s, 3H) 2.33(m, 1H); 1.61(m)+1.39(m)+1.23(br) = 44H. ^{13}C -NMR δ 177.06, 51.24, 45.70, 32.49, 29.52, 29.37, 29.10, 28.91, 27.43.

ADMET/Hydrogenation of methyl 2-(9-Decenyl)-11-dodecenoate (HP5.20).

Elem. Anal. Calcd. for $[\text{C}_{21}\text{H}_{40}\text{O}_2]$: C, 77.72; H, 12.42. Found: C, 77.44; H, 12.43. ^1H -NMR δ (ppm) 3.63(s, 3H) 2.29(m, 1H); 1.54(m)+1.40(m)+1.21(br) = 36H. ^{13}C -NMR δ 177.06, 51.22, 45.71, 32.50, 29.67, 29.57, 29.47, 27.47.

ADMET/Hydrogenation of ethyl 2-(9-Decenyl)-11-dodecenoate (HP5.21). Elem.

Anal. Calcd. for $[C_{22}H_{42}O_2]$: C, 78.05; H, 12.50. Found: C, 77.81; H, 12.49. 1H - NMR δ (ppm) 4.05(q, 2H); 2.38(m, 1H); 1.61(m,)+1.39(m)+1.22(br) = 39H. ^{13}C -NMR δ 176.43, 59.89, 45.67, 32.47, 29.50, 29.36, 29.06, 28.92, 27.43, 14.32.

Synthesis of ADMET model ethylene/vinyl chloride and styrene copolymers

ADMET/Hydrogenation of 11-chloro-1,20-heneicosadiene (HP5.16). Although the ADMET polymerization proceeded in similar fashion to all others, analysis of the polymer after attempted hydrogenation showed very little conversion(virtually unchanged olefin signals in 1H and ^{13}C NMR. The resulting polymer was fully saturated using Pd/C. Unsaturated polymer **P5.16** was dried and degassed by placing under vacuum at 80°C for several hours. Polymer **P5.16** (483 mg) was combined with Pd/C (10% wt/wt, 500 mg) and 15 ml dry, degassed toluene under argon in a pressure tube. The mixture was exposed to a constant 80 psig H_2 at room temperature with vigorous stirring. After 8 hours, the polymer was seen to precipitate as evidenced by gelatinous particles and the Pd/C was no longer freely dispersing. The mixture was heated to 40°C at which time stirring resumed and the gelatinous particles disappeared. After 24 hours, the mixture was filtered through a medium glass frit (while heated) and then passed through a 0.2 μ m syringe filter to insure complete removal of fine Pd/C particles. The water-white solid polymer was obtained in quantitative yield after precipitation into methanol. Elem. Anal. Calcd. for $[C_{19}H_{37}Cl]$: C, 75.83; H, 12.39; Cl, 11.78. Found: C, 75.74; H, 12.51; Cl, 11.68. 1H - NMR δ (ppm) 3.86(m, 1H); 2.02(q, 4H); 1.68(m, 4H);

1.47(m)+1.38(m)+1.23(br) = 32H. ^{13}C -NMR δ 64.39, 38.53, 33.80, 29.70, 29.59, 29.53, 29.21, 26.51.

ADMET/Hydrogenation of 11-phenyl-1,20-heneicosadiene (HP5.17). Elem. Anal. Calcd. for $[\text{C}_{25}\text{H}_{42}]$: C, 87.64; H, 12.36. Found: C, 87.39; H, 12.46. . ^1H - NMR δ (ppm) 7.25(m, 2H); 7.20(m, 3H); 2.43(m, 1H); 1.60(m, 4H); 1.21(br, 32H). ^{13}C -NMR δ 146.43, 128.10, 127.64, 125.64, 46.07, 37.00, 29.79, 29.71, 29.67, 29.57, 27.63.

CHAPTER 3

ADMET DEPOLYMERIZATION OF 1,4 -POLYBUTADIENE UTILIZING A WELL-DEFINED RUTHENIUM CATALYST

Extensive study has been made of the use of olefin metathesis to produce small molecules from unsaturated elastomers where the bulk of the work has focused on reaction of 1,4-polybutadiene (1,4-PB) with substituted olefins as chain transfer agents (CTA).⁵² As discussed in Chapter One, initial studies in this field, just as in all areas of metathesis, utilized ill-defined catalyst systems consisting of some species with sufficient lewis acidity to invoke side reactions such as vinyl addition via cationic pathways. Thus these reactions were termed metathesis degradation rather than depolymerization. With the advent of well-defined catalysts, and more recently classical systems with cocatalysts of diminished Lewis acidity, clean metathesis depolymerization could be achieved.

The reaction is depicted in Figure 3-1, where cross-metathesis of the CTA with the unsaturated linkages of the polymer backbone results in chain-scission and end-functionalization. As in other normal cross-metathesis reactions, the product distribution is governed by statistics. In the event of complete depolymerization, the only products would be diene and excess CTA. In most studies, this has only been achieved with a large excess of CTA. For example, when using the catalyst $WCl_6/Et_4Sn/Et_2O$, 200 equivalents of hex-3-ene were required to achieve above 90% conversion of 1,4-PB to the monomer, deca-3,7-decadiene (Figure 3-1, R = Et, n = 1).²

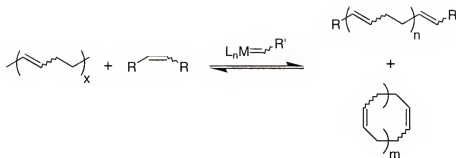


Figure 3-1. Inter- and intramolecular depolymerization of 1,4-polybutadiene.

Unsaturated elastomers may also be depolymerized via intramolecular metathesis to produce macrocycles or oligomeric cyclics. This ring-chain equilibrium, familiar in step/equilibrium polymerizations is affected by temperature, repeat structure, and of course concentration. At sufficient dilution, high molecular weight 1,4-PB may be completely depolymerized to small cyclics (Figure 3-1, $m = 2-8$). In depolymerizations employing CTA's, these cyclics are present in negligible amounts at equilibrium provided CTA/PB repeat unit ≥ 10 . Thus careful control of reaction conditions can determine the position of the equilibrium which is established between the monomeric species, linear and cyclic oligomers, and higher molecular weight species.

Recently, Wagener and coworkers reported the first example of a complete, non-statistical depolymerization of 1,4-PB to monomeric diene using a silane-functional CTA (Figure 3-1, $R = CH_2SiMe_2Cl$, $n = 1$) catalyzed by **1.2b**.^{52o} Approximately 3 equivalents of the CTA were sufficient to achieve this unprecedented observation. Crowe and coworkers later reported⁵³ that allyl silanes function as selective olefin metathesis substrates. Cross metathesis is much more favored between allyl silanes and alkyl olefins than self-metathesis of either class of olefin due to electronic and steric

factors. It may be assumed that this phenomenon is responsible for the above-mentioned non-statistical depolymerization.

Metathesis depolymerization with appropriately functionalized CTA's results in elastomers with reactive end-groups. Hydroxy-telechelic polybutadienes (HTPB) are highly desired due in no small part to their technical utility in polyurethane formulations. Due to the intolerance of most metathesis catalysts for hydroxyl functionality, HTPB's have been prepared by indirect routes where the hydroxyl group is masked during the metathesis reaction. Borane functional CTA's were used in combination with $\text{WCl}_6/\text{Me}_4\text{Sn}$ in one such example (Figure 3-2), where the borane functional telechelics could then be converted under mild conditions to HTPB's.^{52r}

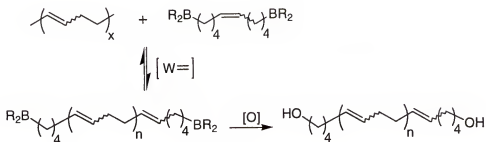


Figure 3-2. Indirect synthesis of HTPB via metathesis depolymerization.

Reports of the broad utility of the ruthenium metathesis catalysts (Figure 3-3) described in part in Chapter One prompted their investigation in metathesis depolymerization chemistry. Of particular significance are their tolerance to functional groups and stability in the presence of ethylene. In this chapter the depolymerization of cis-1,4-polybutadiene with ethylene and with ester-functionalized CTA's catalyzed by **1.4** is described. Observations of the remarkable ability of catalyst **1.4** to effect

metathesis depolymerization of ultra-high molecular weight polybutadiene in the bulk state are also disclosed.

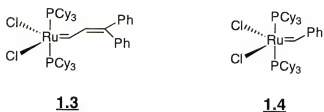


Figure 3-3. Well-defined ruthenium metathesis catalysts.

Ethenolysis of 1,4-Polybutadiene

The cross-metathesis between internal olefins and ethylene was first dubbed as ethenolysis in 1967.⁵⁴ This specific reaction has been the subject of a number of studies and has been exploited commercially.⁵⁵ Applications include the production of ω -unsaturated carboxylic esters from esters of naturally occurring fatty acids and α,ω -dienes from cyclic olefins, shown in Figure 3-4.

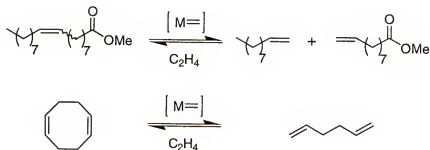


Figure 3-4. Commercial applications of ethenolysis.

The depolymerization of 1,4-polybutadiene, as well as other unsaturated elastomers, via cross metathesis with ethylene catalyzed by the well-defined metathesis catalyst, $[(CF_3)_2CH_3CO]_2(NAr)W=CHC(CH_3)_2Ph$ has been reported.⁵⁶ This reaction

is essentially the reverse of the ADMET polymerization of 1,5-hexadiene, and if the only reaction occurring is ethenolysis, then the principal products would be α,ω -vinyl terminated polybutadiene oligomers (Figure 3-1, R = H). Should conversion be complete, only the monomer 1,5-hexadiene would be produced. Conversions were far from complete, but instead this cross metathesis reaction produced clean oligomers with $M_n = 1,000$ along with trace amounts of 1,5-hexadiene. It was assumed that the low conversions of polymer to pure ADMET monomer were due to inactivation of the catalyst through a previously described competing reaction of the catalyst with ethylene.

Ethenolysis of 1,4-Polybutadiene Catalyzed by a Well-Defined Ruthenium Complex

A polymeric substrate with highly pure microstructure was chosen for these studies (cis-1,4-polybutadiene: 98% minimum cis 1,4-microstructure) (**3.1**) to simplify analysis of product mixtures. A systematic study was performed to determine the effect of ethylene pressure on conversion with all other variables held constant, including **[3.1]/[1.4]**, polymer concentration, solvent and temperature. Solutions of polymer and catalyst in CDCl_3 (**[3.1]** = 2.5M, **[3.1]/[1.4]** = 400) were exposed to a constant pressure of C_2H_4 with vigorous stirring for 48 hours at room temperature, at which time reactions were quenched by slowly bubbling air through the solution. To minimize loss of volatile products, the reaction mixtures were chilled to $T < -50^\circ\text{C}$ and the C_2H_4 was slowly released prior to quenching. The catalyst was removed by briefly stirring with silica gel followed by filtration.

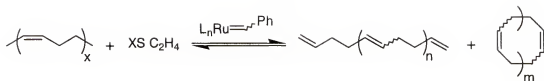


Figure 3-5. Ethenolysis of 1,4-polybutadiene.

Analysis of the product mixtures by GC showed each to be consistently composed of a complex mixture of products, schematically represented in Figure 3-5. GC/MS analysis indicated that major products of these reactions were low molecular weight α,ω -vinyl terminated butadiene oligomers with mass spectral peaks consistently found at $\text{FW} = 82 + n(54)$, where n has the values between 0 and 5. Oligomers with $n > 5$ were not detected. Of course the product with $n=0$ is the monomer 1,5-hexadiene. Trace peaks were identified with mass = $m(54)$ which may be due to cyclic butadiene oligomers.

Due to the complex nature of the product mixtures, individual products were not isolated. A simple alternative is to simply to calculate a relative moment of the product distribution from each experiment to determine the trend in conversion. Therefore, product mixtures were analyzed as a whole by gas chromatography/mass spectrometry (GC/MS) in concert with ^1H and ^{13}C NMR to determine the trend in conversion vs pressure.

The concept of average molecular weight³⁷ is familiar to the polymer chemist as most polymerizations produce not one discrete species with a single molecular weight but instead a homologous series of products characterized by an average molecular weight. One such average, the number average molecular weight (\overline{M}_n), is directly related to conversion for step/condensation polymerizations. Since ethenolysis is the

microscopic reverse of the forward ADMET reaction, a step polymerization, it seems that the most straightforward measure of conversion is to determine \overline{M}_n . \overline{M}_n values were calculated from ^1H NMR end-group analysis and from GC plots and the two values were in good agreement.

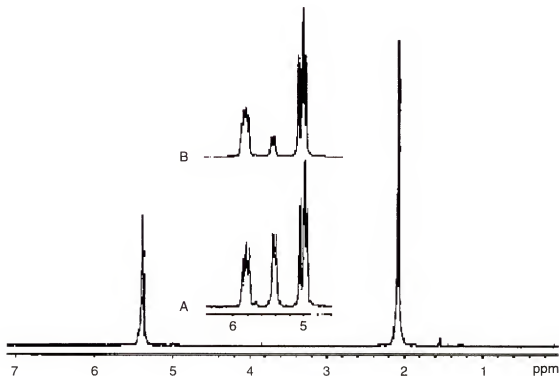


Figure 3-6. ^1H NMR of 1,4-Polybutadiene (**3.1**). Insets are partial spectra of product mixtures from ethenolysis at A: 30 and B: 400 psig C_2H_4 .

NMR spectra of all product mixtures were consistent with α,ω vinyl-terminated butadiene oligomers. Figure 3-6 demonstrates the extent of ethylene depolymerization chemistry. It shows the ^1H NMR spectrum of the reactant, cis-1,4-polybutadiene with peaks near 5.4 and 2.1 ppm corresponding to the olefinic and allylic protons respectively. The insets "A" and "B" are partial spectra obtained from the product mixtures resulting from ethenolysis at 30psig (lowest conversion) and 400psig (highest

conversion) C₂H₄, where the signals centered near 5 and 5.8 ppm represent the terminal and penultimate protons, respectively, of terminal vinyl groups. For mixtures consisting entirely of linear α,ω vinyl-terminated species, number average molecular weights can be calculated using equation 3-1:

$$\overline{M}_n = 108 \left[\frac{I_{io}}{I_{eo}} \right] + 82 \quad \text{Eqn 3-1}$$

where I_{io} and I_{eo} are the areas under the peaks for the internal olefinic protons and terminal vinylic protons, respectively. This method of end-group analysis has been applied successfully to moderately high-molecular weight polymers with well-defined vinyl end groups prepared by the forward ADMET reaction. Since the concentration of other products (cyclics) was low in all cases as determined by GC, this may be considered a reasonably reliable method to follow conversion.

The \overline{M}_n also was estimated from the peak areas of GC plots of each reaction mixture. A representative GC plot for reaction at 400 psig is shown in Figure 3-7 with peaks labeled by their masses determined from GC/MS. No species larger than the tetramer were detected in this case. The trace peaks immediately preceding oligomers have masses, $m(54)$, corresponding to cyclic butadiene oligomers. The trace peaks immediately following major peaks have identical masses as the preceding major peak and are assumed to be linear cis/trans isomers. The relative mass percents of each species (GC) were converted to mole percents then normalized neglecting contribution from solvent and trace peaks due to cyclics. From these values, \overline{M}_n can be calculated using the well-known equation 3-2:

$$\overline{M}_n = \frac{\sum M_x N_x}{\sum N_x} \quad \text{Eqn 3-2}$$

where M_x and N_x equal the molar mass and number of moles, respectively of species x .

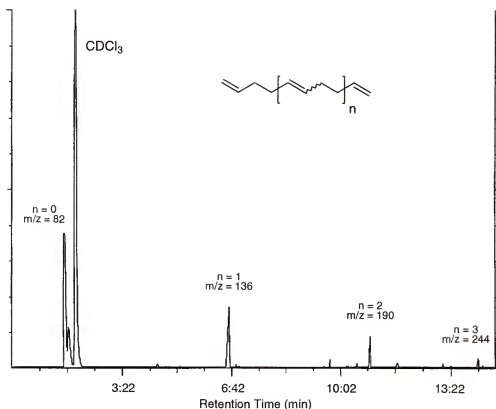


Figure 3-7. Representative GC trace with mass labels (GC/MS). Reaction mixture from ethenolysis at 400 psig C_2H_4 .

The results calculated from 1H NMR and GC are compiled in Table 3-1 along with the relative mole percents 1,5-hexadiene produced as calculated from GC measurements. These results show a general trend in conversion with ethylene pressure with highest conversion of polybutadiene to 1,5-hexadiene being observed at 400 psig C_2H_4 . This may be expected as an increase in ethylene pressure results in an increase in ethylene concentration relative to polybutadiene. That is, CTA/PB repeat unit is

increased, making ethenolysis progressively more favored over self metathesis of polybutadiene.

Surprisingly, beyond 400 psig conversions decrease which could be a consequence of catalyst mortality. Grubbs has reported⁵⁷ that various versions of the complexes **1.4** ($L_nRu=CH-R$, $R = \text{alkyl}$) slowly decompose in solution. He proposed bimolecular decomposition pathways as evidenced by the formation of structures " $R-CH=CH-R$ " in solutions consisting of only catalyst and solvent. The methyldiene, $L_nRu=CH_2$, which is most definitely the catalytic species in ethenolysis, was reported to decompose more quickly in solution; within a matter of hours.

At higher concentrations of ethylene, it may be that non-productive self-metathesis of ethylene begins to offer substantial competition to ethenolysis of the polymer. Further, the probable bimolecular decomposition of the methyldiene could be depleting the system of active catalyst, and these events could lead to the lower conversions observed at higher ethylene pressures. The overall result is an asymptotic upper limit to increasing conversion with increasing ethylene pressure. Similar limiting conversions have been observed in our laboratories in the ethenolysis of low molecular weight 1,2-disubstituted olefins catalyzed by **1.4**.

The identity of trace products with mass = $m(54)$ could not be assigned unequivocally to cyclic cyclic oligomers. Although a trace peak assigned the mass of 108 could be 1,5-cyclooctadiene, the cyclic dimer, an authentic sample of 1,5-cyclooctadiene gave a different retention time from GC.

C ₂ H ₄ (psig)	\overline{M}_n (g/mol)		Mole % (a) 1,5-Hexadiene
	a	b	
30	135	133	43
100	106	114	68
250	99	104	74
400	93	96	82
600	118	128	52
800	122	134	47

Table 3-1. Results of ethenolysis at varied C₂H₄ pressure (a: GC, b: ¹H NMR).

Abendroth⁵⁸ and Thorn-Csannyi⁵⁹ investigated the metathesis degradation of polybutadiene containing substantial amounts of 1,2 linkages. Figure 3-8 shows the cleavage of a 1,4-1,2-1,4 triad from the polymer backbone with hex-3-ene as CTA (R=Et) to form a triene. Subsequent ring closing metathesis yields either of the cyclic products shown. Polymer **3.1**, like all 1,4-polybutadiene produced by chain polymerization of butadiene contains 1,2-linkages. The presence of these irregularities is indicated by a small unresolved multiplet in the ¹H NMR of **3.1** (cf Figure 3-6) at approximately 5 ppm, signifying the terminal CH₂ of pendant vinyl groups. RCM and ethenolysis of these groups, in either order, as depicted in Figure 3-8 (R = H) renders allyl cyclopentene and/or vinyl cyclohexene, both with FW = 108 making them likely candidates for the unknown product. Reexamination of the insets in the ¹H NMR spectra in Figure 3-6 reveals a new small unresolved multiplet at 5.64 ppm which

corresponds well with the olefinic protons of cyclohexene and cyclopentene (both at 5.7 ppm). This small multiplet was observed in the ^1H NMR spectra of all depolymerized **3.1** in this study, and will be discussed further later in this chapter.

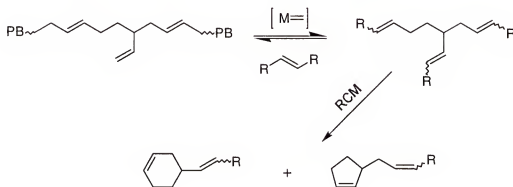


Figure 3-8. Products from extrusion of 1,4-1,2-1,4 triad of PB.

To determine the extent to which **3.1** is intramolecularly depolymerized in the absence of ethylene, a solution of **3.1** and catalyst in CDCl_3 was prepared in the same proportions and concentrations as in the ethenolysis experiments. The PB chunks visibly dissolved much faster (within 30 minutes) than in the absence of catalyst, indicating rapid reaction. The solution was stirred 48 hours then quenched by exposure to air. Silica was used to remove catalyst residue as previously described and the solvent was removed under reduced pressure to yield a viscous liquid. ^1H and ^{13}C NMR were consistent with 1,4-PB but with trans content increased to 81% (quant ^{13}C NMR). The number average molecular weight determined by VPO was 2×10^3 g/mol. This value is not a true measure of the molecular weight produced as any small cyclics would have been removed under vacuum during isolation.

Bulk Depolymerization of Polybutadiene

A remarkable observation was made regarding the solid-state reaction of catalyst **1.4** with polymer **3.1** when the two are placed in intimate contact; in the absence of any other reagents or solvent, the solid polymer begins to liquefy over a period of a few hours! To determine the outcome **3.1** was cut into small chunks and its surface was coated with catalyst ($[\mathbf{3.1}]/[\mathbf{1.4}]=400$), and a magnetic stir bar inserted. During the first few hours of reaction, the mixture was occasionally agitated with a large magnet, until viscosity was sufficiently diminished that slow stirring could be accomplished with a magnetic stir plate. After 24 hours, the reaction was quenched by exposure to air, and the polymer was dissolved in benzene and isolated as described above. ^1H and ^{13}C NMR were consistent with 1,4-PB but with 72% trans microstructure (quant ^{13}C). Characterization of the polymer by GPC indicated a decrease in \overline{M}_n to 9.7×10^3 g/mol (PDI=1.76, monomodal)! Again, any small cyclics, which may have been produced, would have been removed during isolation.

Before discussing the possible route to achieve this depolymerization, the uniqueness of its initiation must first be noted. Evidence suggests during reaction of catalyst **1.4** with olefinic substrates, phosphine must dissociate to free the active site. For metathesis to occur, the catalyst and the polymer must come in contact on a microscopic scale, i.e. the catalyst must dissolve in the polymer. At room temperature, the polymer is above its crystalline melting temperature, T_m of -6°C , and well above its glass transition temperature, T_g of -102°C .³⁷ Under these conditions adequate translational, rotational, and vibrational energies exist to allow molecular motion. This molecular motion together

with the solubility of the catalyst in a range of organic media perhaps is sufficient to allow the polymer to imbibe the catalyst and form a "solid solution" at the interface. The well known molybdenum metathesis catalyst, **1.2b** did not display this reactivity under the same conditions, perhaps due to lower solubility in the polymer.

Assuming the M_n value obtained from GPC for the bulk depolymerized PB is correct within an order of magnitude, the molecular weight of the polymer was reduced by two orders of magnitude ($2\text{-}3 \times 10^6 \rightarrow 9.7 \times 10^3$ g/mol). In the absence of added sources of end-groups, this depolymerization could be considered to have occurred by one or a combination of three metathetical routes: a:) conversion to lower molecular weight macrocycles via intramolecular metathesis, b:) incorporation of the catalyst residues as end groups, and c:) conversion of 1,2-linkages to end groups.

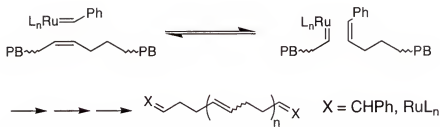


Figure 3-9. Incorporation of residues from **1.4** as end-groups in depolymerization.

The catalyst itself can be converted to end-groups, as depicted in Figure 3-9. Any productive metathesis reaction of the catalyst with the backbone of the polymer causes chain scission. The products are a styryl-terminated PB chain and a ruthenium alkylidene terminated chain. Facile chain transfer of the ruthenium chain end with high molecular weight chains begins the equilibration toward lower molecular weight species. The total number of linear chains should be equal to the total number of catalyst

molecules and therefore the average degree of polymerization equals the repeat unit to catalyst ratio. For this experiment this gives $DP=400$ which corresponds to $\overline{M}_n \cong 2.2 \times 10^4$. Given the inherent error in GPC measurements using dissimilar polymers as standards, this calculated \overline{M}_n agrees within experimental error with that obtained from GPC (9.7×10^3 g/mol).

If conversion of the catalyst to end-groups is the major contributor to this depolymerization, then the outcome should be sensitive to the catalyst loading. The experiment was repeated but with the $[3.1]/[1.4]=4000$, an increase of an order of magnitude. For formation of linear chains terminated by catalyst residues alone, the \overline{M}_n should be over 2×10^5 . Upon quenching by exposure to air, the reaction mixture was characterized without purification to retain any volatile products. The molecular weight distribution in this case was found to be bimodal with the bulk of the sample having essentially the same retention time and profile as the oligomerized PB prepared at higher catalyst loading ($\overline{M}_n = 9.0 \times 10^3$, PDI = 1.72). An additional small peak was detected with retention time indicative of very low \overline{M}_n oligomers, which were probably removed from the first reaction mixture during purification. Because the \overline{M}_n of the depolymerized product was insensitive to the change in catalyst loading, it may be assumed that incorporation of catalyst as end-groups is not the major determinant of the decrease in molecular weight.

As discussed previously, the spacial placement of double bonds in 1,4-1,2-1,4 triads favors formation of cyclopentene and cyclohexene derivatives via ring closing metathesis (RCM). It is proposed here that these imperfections are the major determinant

of the product's molecular weight via the route illustrated in Figure 3-10. RCM of the backbone olefins (bonds a and b) of a 1,4-1,2-1,4 triad extrudes vinyl cyclohexene with relatively infinitesimal decrease in chain size. This molecule however can then act as CTA via cross-metathesis of the vinyl group with the polymer backbone, cleaving the chain. Likewise, RCM of the vinyl group of the triad with an adjacent backbone olefin (bonds a and c) results in direct chain scission.

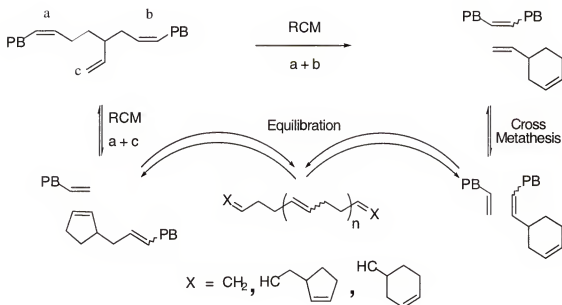


Figure 3-10. Conversion of 1,4-1,2-1,4-triads to end-groups.

Equilibration of the termini toward the most probable distribution should produce polybutadienes terminated by vinyl, cyclohexenyl and cyclopentenyl groups with average molecular weight proportional to the mole percent 1,2 linkages. For example, the production of entirely linear chains via the proposed route from polybutadiene initially containing 0.5% 1,2 linkages would result in $DP = 200$, $M_n = 1.1 \times 10^4$ g/mol. The

presence of the proposed endgroups is supported by the occurrence of the same small unresolved multiplet(5.64 ppm) in the ^1H NMR spectra of all depolymerized samples. Corroborating evidence could be obtained via bulk depolymerization of a series of 1,4-polybutadienes with varying levels of 1,2-linkages.

There is no doubt the increase in entropy associated with conversion of UHMW PB to lower molecular weight macrocycles contributes to this depolymerization. Synthetic ultra high molecular weight polymers may currently only be produced kinetically by capitalizing on the release of energy via events such as alleviation of ring strain or reduction of bond order. This $-\Delta H$ must be sufficiently large to overcome the obvious major $-\Delta S$ inherent in the process of connecting a large number of small molecules by covalent bonds.³⁷ It is essential that no mechanisms exist for reversing the polymerization under the conditions employed. An example of such a mechanism is the thermal depolymerization of polystyrene at or above the ceiling temperature.

ROMP of cyclooctadiene results in an equilibrium mixture consisting of high molecular weight polybutadiene, cyclic oligomers, and monomer. The same equilibrium mixture may be reached whether starting with pure high polymer, pure monomer, or a mixture of all species.² Intramolecular metathesis depolymerization of ultra high molecular weight polybutadiene by conversion to macrocycles provides a thermoneutral route to increase entropy. Once metathesis is initiated in the system reported here, the system should move towards the appropriate equilibrium for this catalyst/polymer combination in the bulk state. Contributions from these processes cannot be excluded.

Bulk Depolymerization of PB to Produce Telechelics

Marmo reported the preparation of moderate molecular weight end-functionalized polybutadienes by metathesis depolymerization utilizing molybdenum catalyst **1.2b**.⁶⁰ Due to the inability of the catalyst to effect cross-metathesis between the CTA and the polymer in the bulk state, a two step process was employed. The polybutadiene was depolymerized by intramolecular metathesis in toluene prior to addition of the CTA, after which the toluene was evaporated to favor the formation of higher molecular weight oligomers at the expense of the cyclics generated during solution depolymerization. In this manner, end-functionalized polybutadienes with $\overline{M}_n = 1.1 \times 10^3$ and 2.6×10^3 g/mol were generated.

The unique reactivity of the ruthenium catalyst with polybutadiene in the bulk state may be exploited to accomplish depolymerizations without the need for solvent. In order to demonstrate the possibilities, polybutadiene was depolymerized by ethenolysis in the bulk state. The polymer was cut into small chunks, intimately mixed with catalyst (**[3.1]/[1.4]** = 400) and agitated until it could be magnetically stirred. Exposure to 100 psig C_2H_4 (48 hours reaction time) resulted in a rapid decrease in viscosity. Analysis by GC and NMR were consistent with the results obtained from ethenolysis in solution. The \overline{M}_n calculated from GC was 147 g/mol, indicating lower conversion than obtained in solution at the same pressure. This is justifiable in terms of relative concentrations, where dilution of PB while maintaining constant ethylene pressure increases CTA/PB repeat unit, favoring higher conversion.

It is highly desired to produce telechelic products consisting entirely of linear chains with each and every chain end containing useful functionality, which may be incorporated via the CTA. This corresponds to a number average functionality (\overline{F}_n) equal 2.0. While competing processes prevent the realization of this ideal case, optimization of reaction conditions can greatly reduce the adverse effect on \overline{F}_n .^{2,41} Polymer chain back-biting producing cyclic species devoid of the desired end-groups may be diminished by using the most concentrated conditions possible. Ill-defined end groups resulting from termination due to catalyst decomposition may be avoided by choosing a robust catalyst, such as **1.4**. The catalyst loading should be kept as low as possible as each catalyst molecule introduces two unwanted end-groups (cf Figure 3-9).

Bulk depolymerization of PB in the presence of CTA should give essentially the same results as the ROMP of COD with CTA. It must however be noted that if the ubiquitous 1,2-linkages are indeed converted to end groups the \overline{F}_n will be adversely affected. Nonetheless, two ester-terminated PB's (ETPB) of differing molecular weights were prepared (Figure 3-11). Ethyl 10-undecenoate (**3.3**) and catalyst ($[\mathbf{3.3}]/[\mathbf{1.4}] = 400$) were combined and placed under vacuum for 24 hours to prepare the dimer (**3.4**). This dimer/catalyst mixture was then added to chunks of PB ($[\mathbf{3.1}]/[\mathbf{1.4}] \geq 4000$, $[\mathbf{3.1}]/[\mathbf{3.3}] = 20$ and 40) and the heterogeneous mixtures were agitated occasionally until stirrable. After 24 hours, the reactions were quenched by exposure to air and the products were dissolved in toluene, stirred with silica and filtered to remove catalyst residue, and the solvent removed under reduced pressure. The molecular weights of the products were characterized by GPC and ¹H NMR, the results of which are summarized in Table 3-2. The values obtained by GPC are higher than the predicted values as expected due to

calibration of the instrument with polystyrene standards. However, the ratio of the measured molecular weights for the two products is approximately the same as the ratio of the predicted values.

Sample	PB/CTA	$(10^{-3})\overline{M}_n$ (g/mol)		
		theory	$^1\text{H NMR}$	GPC [PDI]
<u>3.5</u>	20	1.478	1.5	4.1 [1.76]
<u>3.6</u>	40	2.560	2.6	6.3 [1.70]

Table 3-2. Characterization of ester-telechelic PB's.

The $^1\text{H NMR}$ spectrum of **3.5** is shown in Figure 3-11 along with the reaction scheme. The inset is a magnification of the diminutive signal attributed to the proposed cyclohexenyl and/or cyclopentenyl end-groups created from 1,4-1,2-1,4 triads (cf Figure 3-8).

Conclusions

Catalyst **1.4** has been shown to be highly effective in various types of metathesis depolymerization schemes. Its unprecedented stability in the presence of ethylene qualifies it as a suitable homogeneous catalyst for ethenolysis. The remarkable reactivity of the catalyst with solid polybutadiene allows for the first solvent free depolymerizations of ultra high molecular weight polybutadiene and this method can successively be incorporated into schemes for preparing end-functionalized oligomers.

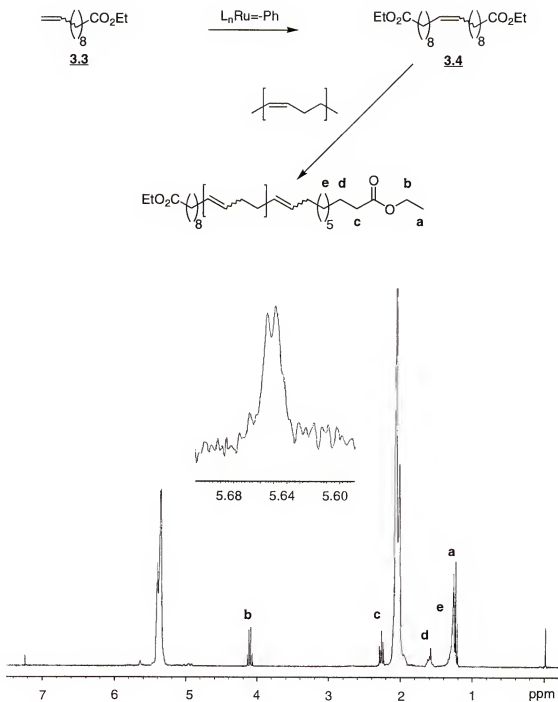


Figure 3-11. ^1H NMR of ester-terminated polybutadiene **3.5**.

CHAPTER 4

TANDEM HOMOGENEOUS METATHESIS/ HETEROGENEOUS HYDROGENATION

Much research has been dedicated to the heterogenization of homogeneous catalysts.⁶² Theoretically, the advantages of homogeneous and heterogeneous catalysis can be combined. Advantages of heterogeneous catalysts include long-lived activity, facile mechanical separation from substrates and products, and recyclability. These attributes have made them highly effective in batch processes common in industry. Homogeneous catalysts often offer greater sight selectivity, greater activity, and operate under milder conditions. Binding a homogeneous catalyst to insoluble substrates may combine the positive aspects of both types of systems. Immobilization produces hybrid heterogeneous catalysts, which are analogous to homogeneous complexes on the microscopic scale. However, industrial research on this topic has decreased dramatically as the desired benefits are seldom realized. Applications are limited by difficulty in preparation, characterization, slower rates, failure to achieve site isolation, and catalyst leaching. Regardless, as the knowledge base in this area increases, this class of catalysts may bear useful systems.

In this chapter, some observations of the reactivity of catalyst **1.4** supported on silica are reported. Preliminary attempts to prepare a well-defined hybrid of **1.4** tethered to silica resulted in the formation ill-defined ruthenium species which are efficient catalysts for olefin migration. This serendipitous observation lead to the realization of a new system for one-pot homogeneous metathesis/heterogeneous hydrogenation. It has been proven effective as a synthetic transform for constructing C-C bonds and in the preparation of saturated aliphatic polymers.

Immobilization of a Well-defined Ruthenium Complex on the Surface of Silica

Catalyst **1.4** is effective in the solution and bulk depolymerization of polybutadiene(PB) to produce functional telechelics. Its robust nature allows good yields of hexadiene through the ethenolysis of PB. However, in the presence of excess C_2H_4 , **1.4** decomposes in solution most likely via bimolecular pathways. If the limiting conversions for ethenolysis, described in Chapter 3, are a direct result then immobilization of the catalyst on a bulky substrate might increase conversions by extending catalyst lifetime. The immobilization of catalysts similar to **1.3** by attachment to crosslinked polystyrene beads via phosphine tethers has been reported⁶³ as shown in Figure 4-1. This hybrid catalyst proved active for the metathesis of 2-pentene and could be recycled. However, turnover numbers were substantially lower than for the homogeneous analogue, which may be attributed to slow diffusion of the substrate and product through the cavities of the tortuous beads.

The adverse effect on rate, due to slower diffusion, might be diminished by attaching the catalyst to the exterior of particles rather inside pores. The method used by Grubbs was modified to tether the catalyst to silica gel particles rather than cross-linked polymer beads (Figure 4-2). Simple chromatographic silica gel was oxidized with piranha wash to increase the surface hydroxyl content and alkyl-bromide tethers were attached by a well known method⁶⁴ for preparing hydrophobic silica. A fraction of the bromide groups were converted to phosphine groups via S_N2 attack by $LiPCy_2$. Reaction with $Cl_2(Ph_3P)_2RuCHPh$ should give the immobilized, well-defined ruthenium complex by displacement of one aryl phosphine ligand by a tethered trialkyl phosphine. The insoluble product was washed repeatedly with toluene to remove any homogeneous species. Grubbs has reported that mixed phosphine versions of ruthenium metathesis catalysts like that proposed here are less active.⁶³ The accepted mechanism for olefin metathesis using **1.4** involves dissociation of one phosphine ligand to provide an open

active site. Should the trialkyl phosphine dissociate in this system, catalyst loading would be lowered (catalyst leaching). It has been shown that trialkyl phosphines have a stronger affinity for the ruthenium center than triaryl phosphines. It was hoped that this tendency could be exploited to decrease catalyst leaching.

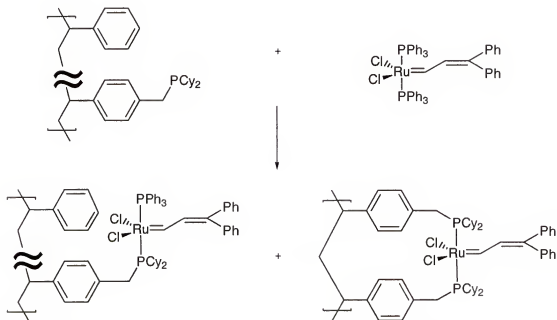


Figure 4-1. Immobilization of **1.3** on cross-linked polystyrene.

To qualitatively assess the metathesis activity of this system, 1-octene was added and the heterogeneous mixture was stirred for 24 hours after which an aliquot was taken for GC analysis. A peak was seen with the same retention time as an authentic sample of *trans*-7-tetradecene, indicating that metathesis had occurred. In addition several other peaks were seen including one with essentially the same retention time as unreacted 1-octene. However, ^1H NMR showed the complete disappearance of resonances from external olefins. Given the low apparent yield of 7-tetradecene and the appearance of various side products, the complete conversion of external olefin to internal olefins must have occurred by competing chemistry other than metathesis.

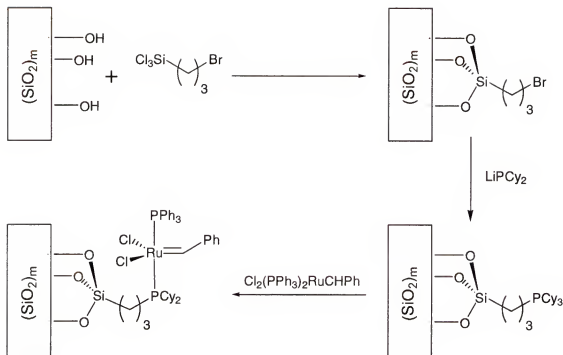


Figure 4-2. Immobilization of ruthenium complex on silica via phosphine tethers.

Catalytic Activity of 1.4 Adsorbed on Silica

Attempts to obtain well-defined, single-site catalysts by tethering sometimes meet with failure due to incomplete coverage of the silica surface with the tethers.⁶⁵ Highly reactive species may then result from deposition of metal complexes and metal particles on the silica surface itself. It was proposed that the side products obtained above might be the result of such competing chemistry.

1-Octene and catalyst 1.4 (0.25mole%) were combined with chromatographic silica gel inside an argon-purged dry box and stirred vigorously 24 hours. The silica gel became reddish-brown and the liquid became colorless signifying that the complex was adsorbed onto the silica surface. ^1H and ^{13}C NMR spectra of the liquid were consistent with linear alkenes with double bonds in internal positions. Analysis of the product mixture by GC/MS showed the presence of a distribution of products with masses

corresponding to a homologous series of straight chain aliphatic alkenes from C_6 to C_{16} . Removal of the product mixture and addition of fresh 1-octene to the heterogeneous catalyst residue gave similar results.

It is proposed that the process for forming this product mixture consists of at least two steps, one of which is olefin migration. Contributing processes may be olefin dimerization.⁶⁶⁻⁶⁹ Figure 4-3 shows dimerization via olefin insertion followed by β -hydride elimination to give dimers, steps that are common to Ziegler-Natta polymerization. With certain catalyst systems, the rate of β -hydride elimination may be fast enough to favor formation of dimers as the major or even exclusive products. Paths A and B differ in the initial regioisomer formed from two different modes of insertion. Olefin insertion into the resulting metal carbon bond may also occur with regioselective competition. The product distribution may be further broadened due to competing regioselective elimination. Only linear products V and VI are consistent with the products obtained using 1.4 adsorbed on silica. The presence of odd carbon species and the absence of branching in the product mixture for 1.4 on silica suggest an alternate mechanism(s). Another possibility is a dimerization mechanism, which proceeds through metallocyclopentanes, but this also gives branched alkenes.

A more likely combination of events is olefin migration in tandem with metathesis as depicted in Figure 4-4. As an example, 1-octene may be isomerized to 2, 3, and 4-octenes through olefin migration. Metathesis of this mixture would result in olefin products ranging from C_2 to C_{14} with the olefins placed from the 1 to the 7 position. Further, the products larger than C_{14} could be formed by olefin migration to the 8 position in any given alkene followed by metathesis. The combination of these two mechanisms results in alkenes with both odd and even number of carbons.

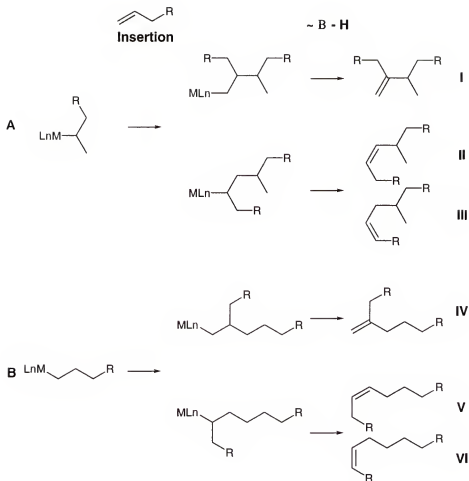


Figure 4-3. Example mechanism for olefin dimerization.

The precatalyst $\text{Cl}_2(\text{Ph}_3\text{P})_2\text{RuCHPh}$ used in the attempted preparation of the tethered catalyst above was evaluated under the same conditions, i.e., adsorbed directly on silica. The unmodified catalyst is not active for the metathesis of acyclic olefins. In concord with the proposed mechanism here, 1-octene was isomerized to a mixture of octenes but no other products were detected. The obligatory metal hydride likely originates from reaction of the ruthenium complexes with silanol groups of the silica. In a related process, ω -unsaturated alcohols are isomerized to aldehydes due to proposed Ru-H species formed *in situ* from reaction of **1.3** with hydroxyl functionality.²⁸ Given the inability of **2** to metathesis acyclic olefins, higher olefins in the tethered system must have been produced by the desired well-defined hybrid version of **1.4**. Metathesis with

1.4 directly adsorbed on the silica is perhaps due to intact metal carbene, which has been simply physisorbed.

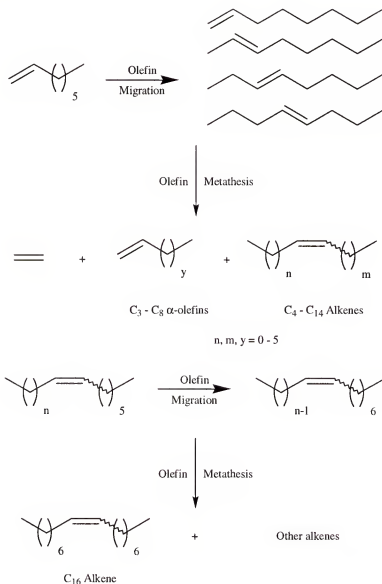


Figure 4-4. Proposed olefin metathesis/migration to produce $\text{C}_4 - \text{C}_{16}$ internal alkenes.

The result of this process may be compared to the overall result of the latter stages of the Shell Higher Olefin Process (SHOP), Figure 4-5.² In the first step, ethylene is oligomerized to α -olefins. These alk-1-enes are isomerized to an equilibrium mixture of internal alkenes. These are then passed over a metathesis catalyst to produce a

statistical distribution of linear alkenes. The C_{11} - C_{14} fraction is separated and the remaining fractions are recycled through the process. The C_{11} - C_{14} alkenes may be converted to detergent alcohols via hydroformylation. The olefin metathesis and isomerization steps might be conducted in one vessel using **1.4** adsorbed on silica. If this system should be proven robust, this could also be a batch process.

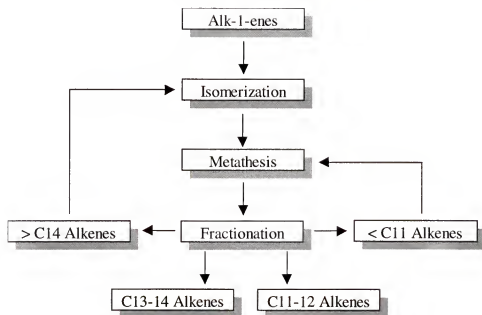


Figure 4-5. Block diagram of later stages of Shell Higher Olefins Process.²

Hydrogenation with the Residue of Catalyst **1.4** Adsorbed on Silica

Catalytic olefin migration and hydrogenation mechanisms have as common intermediates metal hydrides. Ruthenium hydride complexes have been shown to be highly effective hydrogenation catalysts.^{70,71} If this system indeed forms Ru-H species, then it should prove an effective catalyst for olefin hydrogenation. In two separate pressure vessels, *trans*-7-tetradecene and catalyst **1.4** (0.25 mole %) were combined. To one vessel was added 1 g chromatographic silica gel. The two mixtures were stirred for 1 hour and then exposed to 120 psig H_2 for 14 hours with vigorous stirring. 1H NMR

showed the complete disappearance of olefin in the reaction containing silica. The product mixture prepared without silica was less than 30% reduced.

Concurrent with these observations was a report utilizing the residue of a ruthenium metathesis catalyst for hydrogenation. McLain⁷² *et al.* reported a one-pot procedure for producing an ethylene/methyl acrylate copolymer by the ROMP of an ester-functionalized cyclooctene catalyzed by **1.3**, and then hydrogenating by simply applying hydrogen pressure to the completed ROMP reaction system as shown in Figure 4-6. It was assumed that the catalyst residue was converted to $\text{HRuCl}(\text{PCy}_3)_2$. H_2 pressures of at least 400 psi were required to achieve >99% reduction. Lower conversions in the absence of large excess H_2 were contributed to decomposition of the suspected highly unsaturated hydrogenating species. One possible route is the cleavage of solubilizing phosphine ligands via the ubiquitous P-C oxidative addition often seen in transition metal phosphine adducts.⁷³ The result may be species that are not active in hydrogenation and/or precipitation of ruthenium species from solution. Precipitation may result in aggregates with diminished surface area and therefore fewer available reactive sites. Addition of silica may produce ruthenium complexes that are not susceptible to this decomposition pathway. Adsorption of the catalyst residue from a homogeneous solution not only provides for high surface area (more available reactive sites) and diminishes formation of aggregates but also perhaps initiates the reduction by forming the obligatory Ru-H species.

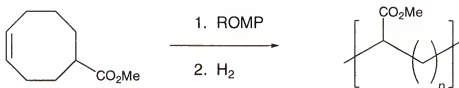


Figure 4-6. One-pot ROMP/hydrogenation to produce model ethylene/acrylate copolymer. Ethylene run length varies ($n = 6, 7, 8$) due to unsymmetrical nature of monomer.

A brief model study demonstrates the effect of varied H_2 pressure on the effectiveness of the heterogenized catalyst **1.4** for olefin hydrogenation. *trans*-7-Tetradecene and **1.4** were combined as above and stirred one hour to allow complete dissolution of catalyst. A change from purple heterogeneous mixture to reddish-brown homogeneous solution indicated dissolution and carbene exchange. Silica was added and the system was exposed to a constant H_2 pressure at room temperature with vigorous stirring for thirty minutes. Conversions were estimated from 1H NMR, comparing the resonances due to the olefinic protons (~ 5.4 ppm) to those of the terminal methyl groups (~ 0.8 ppm). As can be seen from Figure 4-7, reaction can be driven to completion within 30 minutes at low to moderate pressures.

Pressure H_2 (psig)	Conversion
100	41
150	90
200	>99
250	quantitative

Figure 4-7. Hydrogenation of *trans*-7-tetradecene. Conversion estimated from 1H NMR.

This hydrogenation may be incorporated into a two-step, one pot procedure for forming C-C bonds at pressures that are convenient in a laboratory environment without the need for specialized equipment. In the first step, carbon skeletons are constructed via metathesis. In the second step, silica is added to the reaction mixture and the system is exposed to hydrogen to reduce the olefinic product(s), forming the desired C-C single bond. For this procedure to be successful, it is necessary that hydrogen is applied

immediately after addition of silica to preclude homologation via olefin migration and further metathesis catalyzed by the ruthenium residue as it is adsorbed on silica.

To confirm the utility of this process, the olefinic ester **4.1** was dimerized quantitatively by **1.4** (Figure 4-8). Upon completion of the reaction, silica was added and the system was exposed to 120 psig H₂. After mechanical separation of the catalyst residue/silica composite, the long chain α,ω -diacetate **4.2** was obtained in >95% isolated yield.

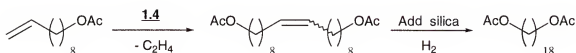


Figure 4-8. Tandem homogeneous metathesis/heterogeneous hydrogenation to produce a long-chain diester.

It has been found desirable by coworkers in our laboratory to prepare bipolar surfactants of the type **4.5** (Figure 4-9) as they can be polymerized using Langmuir trough techniques to produce a 2-dimensional cross-linked network polyaniline. The methodology reported herein was exploited in constructing the long aliphatic segment of **4.5**. The diene **4.3** might be expected to give a mixture of products due to reaction of the styrenic double bond (bond b) in addition to the α -olefin (bond a). As predicted based on recent reports of selectivity in the metathesis of substrates with varied electronic and steric modifications, bond **b** is unreactive under the conditions employed for metathesis catalyzed by **1.4**. Crowe⁵³ investigated the reactivity of olefins with varied steric and electronic modifications including allyl silanes, acrylonitrile, and styrenes, where cross-metathesis of these substrates with alkyl olefins proved to be selective. β -Alkyl styrenes

were also shown to be of lower reactivity. Perfluoroalkyl and some fluoroalkyl substituted olefins have also been shown to be inert towards catalyst **1.4** due to lowered electron density of the double bonds. Bond **b** of substrate **4.3** also proved to be unreactive at room temperature in the presence of **1.4**. Not only is it sterically crowded, but the electron density of bond **b** is diminished by the nitro-substituted benzene ring. As a result, triene **4.4** can be obtained in 95% isolated yield after flash chromatography.

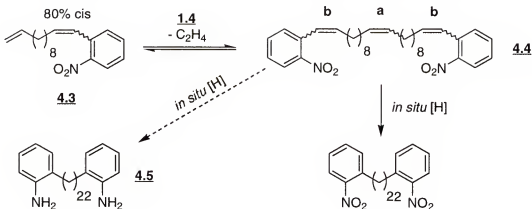


Figure 4-9. Attempted synthesis of bipolar aniline surfactant.

In situ hydrogenation of **4.4** revealed some aspects of relative selectivity of the system reported here. Hydrogenations were conducted at room temperature (24 hrs) and conversions were estimated from ^1H NMR. At 120 psig H_2 , bond **a** is quantitatively hydrogenated. However, bond **b**(cis) is only converted by approximately 90% while **b**(trans) is virtually unreacted. At 800 psig, conversions are near quantitative and approximately 80% for **b**(cis) and **b**(trans), respectively. This is in keeping with the selectivity typically observed in the hydrogenation of sterically hindered cis/trans isomers. In both cases, trace peaks were detected (^1H NMR) which might be assigned to the aniline moiety resulting from reduction of the nitro group. Reports of hydrogenation with

various homogeneous catalysts of general formula $\text{Cl}_n(\text{R}_3\text{P})_m\text{RuL}_n$ indicate pressures in excess of 80 atm are required to obtain good to excellent conversion of aromatic nitro compounds to aniline derivatives in practical reaction times.⁷⁴ Optimization of reaction conditions might allow higher conversion in hydrogenation of nitro-functionalized substrates providing an indirect route to primary amines without the need for protection/deprotection schemes.

Preparation of Saturated Polymers by Tandem Homogeneous ADMET/ Heterogeneous Hydrogenation

Olefin metathesis polymerization has proven to be quite broad in scope for the preparation of well-defined polymers and hydrogenation of these provides additional polymers with unique microstructures.⁴⁶⁻⁵¹ Hydrogenation also produces new polymers with differing physical and chemical properties, including greater oxidative stability. These syntheses typically involve first the synthesis and separation of unsaturated polymers from the metathesis catalyst followed by a second hydrogenation step. Hydrogenated polymers from norbenene and derivatives of norbornene have been produced commercially as Zeonex™ since 1991.

Preparation of End-Functionalized Polyethylene by ADMET/Hydrogenation

A useful application of metathesis/hydrogenation is the production of commercially valuable telechelic polyethylenes. This has been demonstrated in the production of hydroxy-telechelic polyethylene via diimide reduction of intermediate telechelic polyalkenamers.⁶¹ The polyalkenamers were produced through ROMP of

cyclooctadiene in the presence of 1,2-disubstituted olefins, as described in Chapter Three. Similar polyalkenamers may be produced by ADMET polymerization in the presence of functionalized CTA's.

The new tandem homogeneous metathesis/heterogenous hydrogenation technique utilizing catalyst **1.4** proved effective for preparing end-functionalized polyethylene (**4.6**) (Figure 4-10). 1,9-Decadiene was polymerized using **1.4** under typical ADMET conditions in the presence of 0.2 equivalents 9-decenyl acetate (**4.1**) as a chain transfer agent. Subsequent heterogeneous hydrogenation requires the addition solvent to aid dispersion, but dilution in the presence of active metathesis catalyst would favor formation of lower molecular weight cyclics at the expense of linear species. Therefore, the polymer was intimately mixed with silica and the system was exposed to 120 psig H₂ for 30 minutes prior to addition of toluene. Extensive hydrogenation had already occurred at this point to yield a product with sufficient polyethylene character to render it poorly soluble in toluene. Hydrogen pressure (120 psig) was reapplied for five hours while heating in a 90°C oil bath to prevent precipitation of the product. Simple hot filtration and removal of the solvent under reduced pressure yielded a water-white solid in near quantitative yield.

Molecular weight measurements agree well with the value predicted $\overline{M}_n = 1.5 \times 10^3$ g/mol based on the ratio of chain limiter to diene in the ADMET reaction. End-group analysis (¹H NMR) and high temperature GPC (vs PE) gave 1.5×10^3 and 1.7×10^3 g/mol, respectively. The polydispersity (1.9) approaches that expected for equilibrium condensation polymerization. Examination of the ¹H NMR spectrum (Figure 4-10) in the region from 4.8 – 6.0 ppm reveals good conversion in the hydrogenation step, as

indicated by complete disappearance of signals arising from olefinic protons. Acetate content of the product as calculated from ^1H NMR did not decrease from that expected from initial stoichiometry indicating that these groups remain intact throughout the olefin hydrogenation. This reaction was repeated, with aliquots periodically removed to qualitatively assess the time required for complete reduction. By ^1H NMR, signals due to olefinic protons completely disappear within 4 hours.

Synthesis of a Polyester with Long Aliphatic Segments

Pennelle⁷⁵ and coworkers reported the synthesis of a polyester with regular long alkyl segments within the polymer backbone by classical condensation of a long chain aliphatic diol with a diacid (Figure 4-11). Their interests lie in the control of lamellar crystal structure by introducing regular defects in a polymer with high polyethylene character.

Similar polymers may be constructed by the ADMET/hydrogenation method reported here as illustrated in Figure 4-12. The ester diene (**4.7**) was condensed by ADMET and the polymer was hydrogenated as described previously in this chapter for hydrogenation of end-functionalized polyoctenamer. The higher molecular weight and crystallinity of the unsaturated polyester (**4.8**) slows its dissolution in toluene, allowing the addition of solvent just prior to exposure to hydrogenation without fear of rapid metathesis depolymerization. The saturated polyester (**4.9**) was obtained as a white solid in near quantitative yield. The structure shown is not entirely correct as the ester groups may be incorporated in head-head, head-tail, and tail-tail distribution, a consequence of the unsymmetrical nature of the ester moiety.

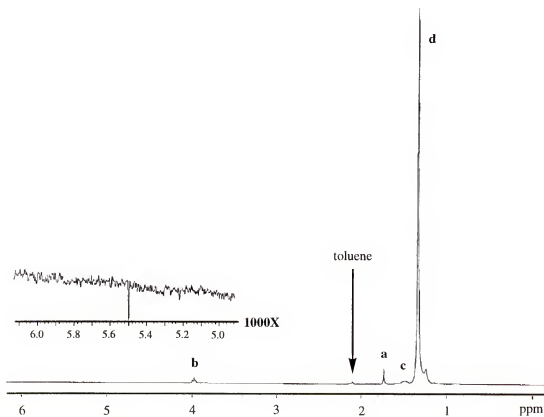


Figure 4-10. ^1H NMR of telechelic polyethylene from ADMET/hydrogenation.

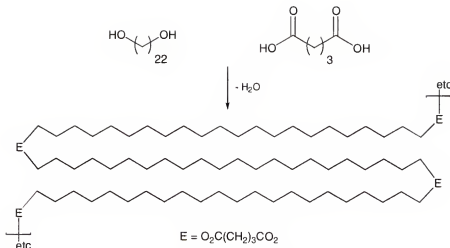


Figure 4-11. Preparation of a polyester with long ethylene run lengths by classic condensation chemistry.

The ^1H NMR spectra for polyesters **4.8** and **4.9** are shown in Figure 4-13. Due to its highly crystalline nature ($\Delta H_f = 122 \text{ J/g}$, $T_m = 97^\circ\text{C}$, DSC) and long ethylene run lengths, polymer **4.9** displays very limited solubility in typical organic solvents at room temperature, but is freely soluble above 60°C . Thus NMR measurements for this polymer were acquired at 90°C in toluene- d_8 which apparently also increases resolution of the overlapping signals corresponding to the protons β to the ester group ("a" and "d"). Note the signals ("g", upper and "e", lower) indicating conversion of vinyl ends groups of polymer **4.8** to methyl end groups upon hydrogenation. High temperature GPC (vs polyethylene standards) gave $\overline{M}_n = 1.0 \times 10^4 \text{ g/mol}$ (PDI = 1.7) for polymer **4.9** and these values agree within experimental error with those obtained for **4.8** under the same conditions.

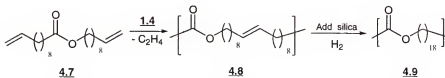


Figure 4-12. Preparation of saturated aliphatic polyester by ADMET/hydrogenation.

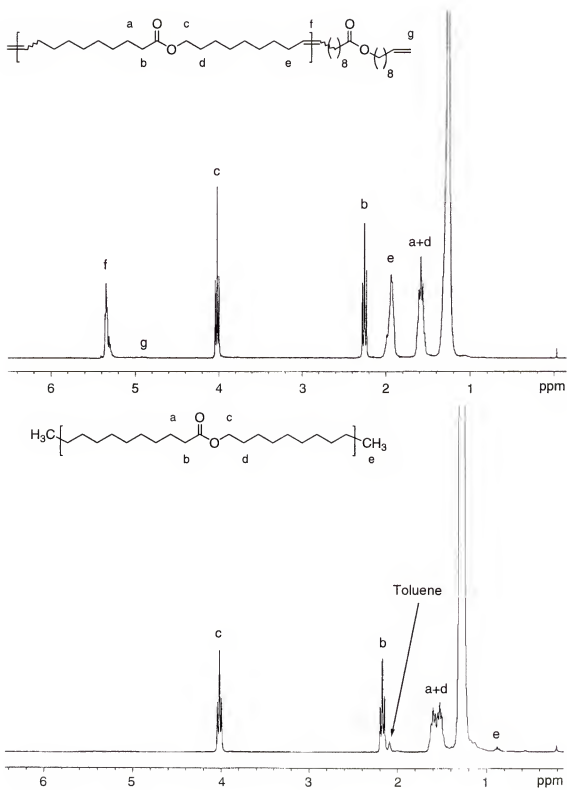


Figure 4-13. ^1H NMR spectra of **4.8** (upper, CDCl_3) and **4.9** (lower, toluene-d_8 , 90°C).

Conclusions

The method reported herein is a facile one-pot route for forming carbon-carbon bonds in the synthesis of polymers and small molecules. No additional catalysts or reagents are needed for hydrogenation other than inexpensive silica gel and hydrogen gas. Addition of silica as a support for the ruthenium complex not only facilitates hydrogenation at low to moderate pressures but also simplifies purification of products. No purification step is required prior to hydrogenation and the catalyst may be removed by simple mechanical filtration. It shows promise both commercially in the preparation of telechelic polyethylenes and in the preparation of model polymers.

The ester moieties of the polymers in Figures 4-11 and 4-12 can be easily incorporated into polymer backbones with long ethylene run lengths by classical ester condensation chemistry. However, other functional groups that may provide deeper insight into the engineering of crystal structures may prove difficult or even impossible to incorporate into a high molecular weight polymer. The method of ADMET/hydrogenation is very well suited to producing model polymers of this type, as symmetrical dienes with a wide variety of functional groups at their center may be constructed by typical organic transforms. The method for incorporating the functional group into the polymer is the same mild procedure regardless of constitution. Applications of this process to the preparation of such model “functionalized polyethylenes” will be described in the following chapter.

CHAPTER 5
THE SYNTHESIS OF MODEL ETHYLENE/POLAR MONOMER
COPOLYMERS VIA ADMET AND HYDROGENATION

Since macromolecular compounds are, almost without exception, polymolecular mixtures, one does not deal with uniform materials, as is the case for low molecular compounds. In the most favorable case, such a material is polymeruniform, that is, a mixture of macromolecules of the same structure, but different chain lengths.

Hermann Staudinger⁷⁶

Flawless control in the construction of discrete molecules of high molar mass has been exhibited only in nature, where the macromolecular engineer and the legislator of laws governing the implication of chemical transforms are one and the same. The indispensability of this level of control is demonstrated by the horrendous outcome of rare mistakes in these biological polymerizations. DNA, one of the many forms of natural polymers, stores coded information in its perfect sequences of nucleic acid repeat units and these codes are read and used to replicate the perfect polymers as well as to produce others.⁷⁷ Numerous cancers, birth defects, and diseases are now linked to what are errant polymerizations induced by mutated DNA or misreading of its codes.

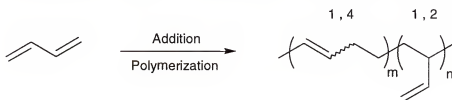
Man's clear mediocrity in this arena is demonstrated by current practices to combat the polymerizations gone awry. These include "shotgun" approaches such as chemotherapy and radiation treatments, with their well-known grim physiological side effects due to the indiscriminate statistical termination of both properly and improperly functioning polymerizations. All modern synthetic schemes are governed to some extent

by statistical elements, limiting the control which chemists may exert over the outcome of their chemical products, including polymers. Man's subjugation to statistics has even prompted some to ascribe the development of nature's perfect polymerizing machines to a statistical process termed evolution.

With regard to chemical homogeneity, the aesthetic simple structures assigned to synthetic polymers are rarely accurate depictions. For example, even in the absence of side reactions such as chain transfer and termination, butadiene may be incorporated into a polymer backbone via chain polymerization in numerous regiochemical and stereochemical modes of propagation³⁷ which are certainly not adequately represented by the single generic structure depicted in Figure 5-1. The monomer may be incorporated into the chain in 1,4 (both *cis* and *trans*) and 1,2 fashion and sequences of 1,2 repeats may also display varying degrees of tacticity. An example of a highly efficient near perfect polymerization is Zeigler-type polymerization of butadiene with Neodymium catalysts by which ultra-high molecular weight polybutadiene, i.e., on the order of 10^6 g/mol may be prepared with 1,4 content as high as 99.5% ($\geq 98\%$ *cis*).⁷⁸ This is truly an amazingly well controlled reaction as any organic chemist would be thrilled to conduct transforms yielding crude product mixtures that are 99.5% pure. However, in this case, the 0.5% 1,2 units cannot be removed from the product mixture as they are covalently bound to the pure portion of the product. By comparison with small molecule chemistry, while the bromination of butadiene may afford a mixture of products where 1,2 and 1,4 addition compete, distillation, chromatography, or a combination may separate the desired product.

While pure polymer microstructure is not a prerequisite for technical utility, the availability of polymers with progressively greater chemical homogeneity has allowed deeper insight into structure/property relationships. With judicious choice of catalyst and monomer, ADMET polymerization has been shown to produce polymers with pure microstructure within spectroscopic detection limits. The combination of the clean ADMET polymerization with mild chemoselective olefin hydrogenation has been shown to be an effective method for preparing model polymers that are polymer uniform. The realization of the facile one-pot procedure for ADMET/hydrogenation reported in Chapter 4 served to streamline this process for producing model polymers. The remainder of this chapter describes the use of this process to prepare models for copolymers of ethylene with vinyl monomers including vinyl acetate, vinyl chloride, styrene, and acrylates and subsequent preliminary thermal analysis of these polymers. A brief description of the commercial polymers for which these polymers serve as models is first given in order that the reader may grasp the significance of the results reported here.

Polymerization: Products from different modes of addition inseparable



Bromination: Products from different modes of addition easily separable

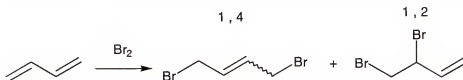


Figure 5-1. Macromolecular versus small molecule chemistry of butadiene.

Ethylene/Polar Monomer Copolymers

Polyethylene has been produced commercially since 1942⁷⁹ and has grown to be the world's largest volume commercial polymer.⁸⁰ A multitude of grades exist, depending on the method of manufacture, with varying molecular weights and levels and types of branching granting a broad scope of properties. Variation of the polymer constitution via copolymerization of ethylene with various substituted ethylenes dramatically increases the range of new materials.

Commercial products in the class of ethylene/polar monomer copolymers include as comonomers vinyl acetate, acrylates, acrylic acid, etc. Inclusion of vinyl acetate or acrylates, for example, yields products with decreased crystallinity and increased room temperature flexibility, impact resistance, and optical clarity relative to ethylene homopolymer. Variation of the comonomer content also greatly effects properties allowing application of EVA in such diverse end uses as packaging films, gloves, squeeze toys, and hot-melt adhesive formulations.³⁷

Ethylene/polar monomer copolymers are produced commercially by the same high-pressure free radical processes utilized for low density polyethylene. As a result of the nature of the free radical polymerization, the polymer microstructures are ill-defined with uncontrolled branching and broad polydispersities due to chain transfer reactions. Branching can occur via hydrogen-atom extraction (chain transfer) by the propagating chain end both intra- and intermolecularly. The former leads to short chain branching (SCB) while the latter leads to long chain branching (LCB) as shown schematically in Figure 5-2.

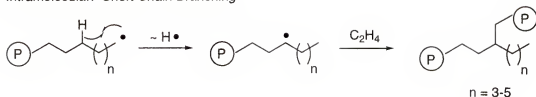
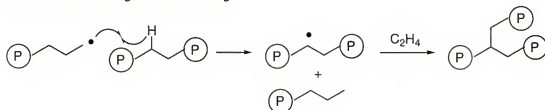
Intramolecular: Short Chain Branching*Intermolecular: Long Chain Branching*

Figure 5.2. Origin of SCB and LCB in free radical polymerization.

Some polar monomers contain hydrogen atoms which are more easily abstracted and therefore copolymers containing these have a higher degree of branching. For example, both the methine proton of the vinyl acetate repeat unit and the methyl protons of the acetoxy group in either the monomer or the repeat unit provide sites for additional branching.⁸²

The microstructures of these copolymers are further complicated by statistical incorporation of the comonomers into the polymer backbone. The comonomers may be incorporated in different amounts according to their relative concentrations and reactivities. The sequence distributions may also vary between alternating, blocky, and random as governed by the product of the monomer reactivity ratios r_1 and r_2 as defined below. For a system consisting of two monomers, M_1 and M_2 , k_{11} is the rate constant for a chain ending in M_1 adding to monomer M_1 , k_{12} is the rate constant for a chain ending in M_1 adding to monomer M_2 , and so on.

$$r_1 = \frac{k_{11}}{k_{12}} \quad r_2 = \frac{k_{22}}{k_{21}}$$

For $r_1 \approx r_2 \equiv 0$, the monomers tend to be incorporated in an alternating fashion where each M_1 is followed by M_2 and vice versa. When $r_1 > 1$, $r_2 > 1$, the chain end has a higher tendency to add to the monomer from which it was derived resulting in blocks, or extended sequences, of each monomer. In the case of $r_1 r_2 \equiv 1$, the polymerization is termed an ideal polymerization and the two monomers are incorporated in a random fashion. This is generally the case for ethylene vinyl acetate, ethylene/acrylate and some other commercial ethylene polar monomer pairs in the typical temperature/pressure regimes used in commercial free radical copolymerizations.

Among commercial polar monomer copolymers with differing comonomers there is broad variability in the molecular weights, PDI's, branch content and identity, and sequence distributions. Model copolymers with less variable microstructure should greatly ease the evaluation of structure/property relationships. The preparation of such models will be described in this chapter.

Model Polymers

“The term ‘model polymers’ in its modern meaning now refers to samples with often complex architectures in which fluctuations in size, structure, composition, or functionalization are minimal.”⁸³ A polymer chemist, mindful of the limitations of modern synthetic chemistry, penned this definition including the key word “minimal”. The production of model polymers requires 1) a mechanistic route that is free of competing chemistry and is long lived, 2) each and every monomer unit must be incorporated in precisely the same fashion, and 3) reaction must be site-specific in that

intended spectator functionality in the monomer remains as such. In short, only one mechanistic event may occur.

Typical routes used to prepare model polymers include living chain polymerizations utilizing ionic, radical, and group transfer chain techniques which have been optimized to limit chain transfer, termination, and other side reactions to maximize control of the primary structure. These modifications have allowed the construction of polymers with narrow polydispersity and of block copolymers with relatively uniform block lengths. However, it must be noted that even for polymers with perfect microstructure and extremely narrow polydispersity, $PDI \leq 1.03$, one has but to observe a MALDI spectrum to recognize that the products are still chemical mixtures of homologous polymers.⁸⁴

The synthesis of discrete macromolecules has only been achieved by stepwise synthesis where the building blocks are connected one at a time and the resulting product is isolated and purified after each connection.⁸⁵ Now prolific examples of this repetitive approach to macromolecular engineering are the three dimensional dendrimers.⁸⁶ This repetitive approach has been utilized⁸⁷ to prepare discrete polyalkenamers (Figure 5.3) identical in repeat structure to polydisperse samples which might be prepared through the ADMET or ROMP of 1,13-tetradecadiene and cyclododecene, respectively. The “dimer” is prepared by Wittig reaction after which the product is isolated and divided into two portions. One portion is hydrolyzed to the aldehyde and the other is converted to the Wittig salt. These may be reacted together and the sequence of events is repeated, each time doubling the degree of polymerization.

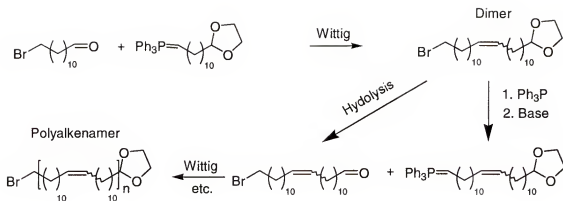


Figure 5-3. Repetitive approach to synthesis of polyalkenamers.

Preparation of Model Polymers via Metathesis

For the purposes here, the definition for model polymers provided at the beginning of the previous section shall be modified. These shall include polymers synthesized by alternate methods to obtain a primary structure similar to existing polymers but greater chemical homogeneity than is obtainable by traditional means.

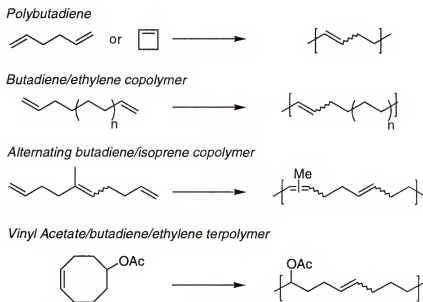


Figure 5-4. Synthesis of model polybutadiene and butadiene copolymers.

A few examples, illustrated in Figure 5-4, serve to demonstrate the utility of metathesis polymerizations in preparing models for polybutadiene and its copolymers. Purely linear, branch-free polybutadiene with 100% 1,4 microstructure may be prepared by the ADMET of 1,5-hexadiene or the ROMP of cyclobutene, 1,5-cyclooctadiene, 1,5,9-cyclododecatriene, etc. Polymerization of monomers with a greater number of methylene spacers between the double bonds produces models for sequence-ordered copolymers of ethylene and butadiene where the exact frequency of unsaturated sites (butadiene repeat unit) is governed by the number of methylene spacers in the monomer. A strictly alternating butadiene isoprene copolymer has also been prepared⁸⁸ in this manner as shown in Figure 5-4. It must be noted that due to the unsymmetrical nature of the monomer, the isoprene units may be incorporated in 1,4 or 4,1 fashion; the methyl substituent may be in the 2 or 3 position of the isoprene unit. In an analogous example utilizing ROMP, Hillmyer⁶¹ prepared a model butadiene, ethylene, vinyl acetate terpolymer by the ROMP of 5-acetoxy cyclooctene. In both of the last two examples, the number of carbons separating the carbon with a pendant substituent varies between 6, 7, and 8. *This introduces the important caveat that the production of polymers by these methods with perfect repeating sequences requires the use of symmetric monomers.*

Model Polymers via Metathesis Polymerization and Hydrogenation

The only variable in the repeat structure of ADMET homopolymers is the cis/trans ratio of the backbone olefinic bonds. Coupling of ADMET polymerization with a clean, quantitative olefin hydrogenation technique constitutes a viable synthetic method to produce polymers with perfect repeating sequences. This was first demonstrated⁸⁹

whereby polyoctenamer was fully saturated utilizing stoichiometric diimide reduction to a perfectly linear, branch-free model for the largest volume industrial polymer, polyethylene (Figure 5-5). The key to this successful, clean hydrogenation was the addition of a bulky amine base, tripropyl amine, to prevent side reactions induced by a known side product, p-toluene sulfonic acid. A polyethylene with narrow polydispersity was later produced⁹⁰ by hydrogenation of a polybutadiene obtained via the ROMP of cyclobutene.

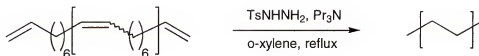


Figure 5-5. Production of perfectly linear polyethylene via ADMET/hydrogenation.

This method was later extended to prepare models to study branching in polyethylene.⁵¹ Symmetrical dienes like that shown in Figure 5-6 were condensed by ADMET and then hydrogenated by the diimide reduction. The microstructure of the resulting polymers is essentially the same as polyethylene with regularly spaced methyl branches, where precision in the sequence distribution of methyl substituents is granted by the nature of the ADMET reaction. The frequency of the methyl branches is prescribed by the value of “n” which may easily be varied during monomer synthesis. These polymers and others like them may serve as useful models to study polymer crystallization, as more in depth studies follow.

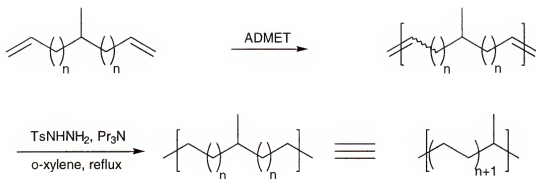


Figure 5-6. The synthesis of model “polyethylene” with regular methyl branches.

Similar polymers have been prepared via hydrogenation of alternating butadiene/ α -olefin copolymers obtained by Ziegler-type polymerization.⁹¹ While the frequency and chemical identity of branching is highly controlled, the only possible frequency of branching is one branch on every 5th carbon. Attempts to prepare models with lower count frequency by chain techniques results in random placement. This introduces a second important caveat in these modeling studies: *Model polymers with “long” linear aliphatic segments of precise lengths are most conveniently prepared by condensation chemistry.* Further, ADMET condensation chemistry is perhaps currently the most general method, allowing the macromolecular engineer to dictate the precise length of the hydrocarbon segment as well as the incorporation of a broad range of functionality into the backbone or as pendant groups.

A simple retrosynthetic analysis (Figure 5-7) of the generic model polymer teaches this point. The target polymers have repeat units with precisely defined aliphatic segments separated by functional groups “Z”. Utilizing classical polycondensation chemistry the polymer can be prepared from the bifunctional monomers shown where “X” and “Y” are reactive functional groups which condense to form the desired functionality “Z”. This approach will be sufficient for polymers such as polyesters ($Z =$

CO_2 ; $X, Y = \text{CO}_2\text{H}, \text{OH}$) where the associated chemistry has been well delineated and applied commercially for many years. Due to the relation between conversion and \overline{M}_n in condensation chemistry, the types of functionality “Z” that may be substituted for ester is limited to only those groups that may be constructed in very high yield.

To illustrate the value of the ADMET/hydrogenation approach in preparing these type models, we need only to attempt to design a synthetic route for the same type polymer but substitute any functional group “Z” for which polycondensation chemistry has not been proven so effective. For example, should it be desired to prepare a polyether ($Z = \text{oxygen}$), low molecular weight oligomers might be produced by reaction of a long chain dialkoxide ($X = \text{OLi}$) with a dihalide ($Y = \text{Br}$), but the limiting yields of this reaction would not allow production of high molecular weight polymers.

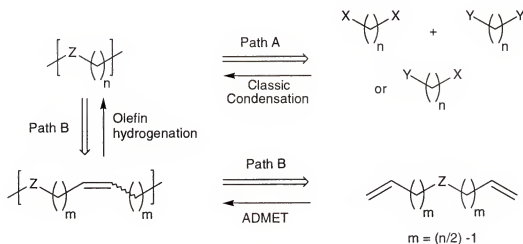


Figure 5-7. Classic condensation chemistry versus ADMET/hydrogenation to prepare model polymers with long, defined aliphatic segments.

Instead, the ether moiety could be incorporated into a long chain diene by the Williamson ether synthesis and then this monomer condensed to high molecular weight by ADMET; hydrogenation then provides the desired polyether. Regardless of the

identity of Z, the polymerization proceeds to high conversion, provided that Z is compatible with the metathesis catalyst. This approach should be quite general as ADMET chemistry has been proven effective for the polymerization of dienes containing a wide variety of functionality.³⁶ Some examples of polymers prepared by ADMET/hydrogenation are shown in Figure 5-8.

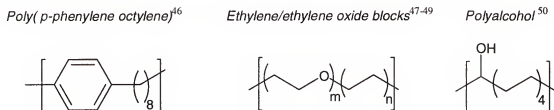


Figure 5-8. Examples of model polymers produced by ADMET/hydrogenation.

Design and Synthesis of Symmetrical Diene Monomers for Ethylene/Polar Monomer Model Polymers

The preparation of ADMET model ethylene/polar monomer copolymers hinges on the availability of highly pure dienes with relevant functionality. A series of symmetrical dienes with central pendant functionality were prepared with varied functionality and number of methylene spacers separating the functionality from the olefin groups. These were obtained in sufficient purity that contaminants could not be detected by NMR, GC, and HPLC.

Central starting materials in nearly all synthetic schemes used to prepare ADMET monomers have been ω -alkenyl bromides. They are versatile reagents in that they can serve as alkylating agents (electrophiles) and as nucleophiles when converted to Grignard reagents allowing for the synthesis of a broad range of dienes. These starting materials

are commercially available with varied number of spacers between the terminal alkene and bromo functionality. In all previous ADMET studies, it was not the focus to prepare polymers with “very long” aliphatic segments. However, as the target polymers reported here are to have long aliphatic segments it was necessary to prepare longer dienes, through chain extension of commercially available ω -alkenyl materials. Decenyl and undecenyl bromide are the longest commercially available starting materials but were found to be contaminated by regioisomers (internal olefin) which could not be removed in a practical manner. The consequence of using these starting materials would be unsymmetrical placement of the double bonds about the central pendant group of the diene monomers and consequently irregularity in the periodicity of the polymer.

Commercially available synthons for these starting materials are decenol, undecenol, and undecenoic acid, which are free of detectable regioisomeric impurities. Many means are available in the literature for the conversion of alcohols to bromides however a mild method must be chosen here to avoid reaction with the terminal olefin. The least expensive and simplest techniques, utilizing PL_n/Br_2 , PBr_n , or HBr as the Br^- source can result in the unwanted side reactions of hydrobromination and bromination of the terminal olefin. The ω -unsaturated alcohols may easily be converted to the bromide by either of two very mild methods, both in good to excellent yields, as shown in Figure 5-9. In the first method, the alcohol is tosylated and then converted to the bromide after only simple aqueous workup without the need for further purification. The second method utilizing $\text{PPh}_3/\text{CBr}_4$ achieves the conversion in comparable yields in one step. Both reactions are highly atom-inefficient but are facile and typically afford the bromides in high isolated yield and purity after distillation.

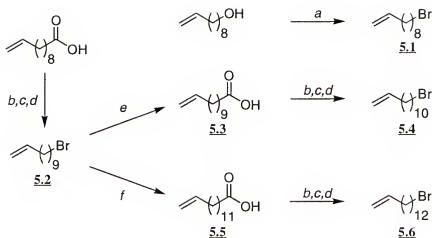


Figure 5-9. Syntheses of ω -unsaturated carboxylic acids and bromides. *a*: Ph₃P,CBr₄. *b*: LAH. *c*: TsCl, pyr. *d*: LiBr, acetone. *e*: ①Mg, ②CO₂. *f*: ①Mg, ② CuCl, β -propiolactone.

These alkenyl bromides were chain-extended by reaction of their Grignard salts with CO₂ or β -propiolactone. In the second case, the addition of catalytic Cu(I) favors nucleophilic attack at the methylene adjacent to the ring oxygen over attack at the carbonyl carbon. These synthetic fatty acids may not be purified on a large scale by the classical method of extraction into basic aqueous solution as they are of sufficient length to act as surfactants producing intractable emulsions under typical isolation conditions. They instead are purified by distillation or flash chromatography. These acids were reduced to the alcohols with excess LAH and then converted to the corresponding chain-extended bromides via the tosylate as above. Conversion of the bromides to the chain extended alcohols, transforms *e* + *b* or *f* + *b* in Figure 5-8, could also each be achieved in one step by substituting formaldehyde and oxirane, respectively, for CO₂ and β -propiolactone. However, the ω -unsaturated acids are useful starting materials for preparing additional dienes as will be discussed later.

Synthesis of Acetoxy-Functional Monomers

A series of symmetrical dienes with central pendant acetoxy groups (Figure 5-10) was synthesized with the goal of preparing model ethylene/vinyl acetate copolymers. The shortest acetate-functional diene (**5.12**, $n=8$) was prepared by a four-step procedure, due to the very low cost of starting material, and the ease of the steps. The first three steps were conducted with aqueous extraction as the only workup. The secondary alcohol was purified by flash chromatography as acetylation without prior purification produced a mixture with impurities that could not be practically separated from the target acetate monomer. The remaining secondary alcohols ($n = 9, 10$ and 12) were prepared in good yields in one step via reaction of *in situ* formed alkenyl Grignard reagents with methyl formate, after which acetylation provided the desired monomers.

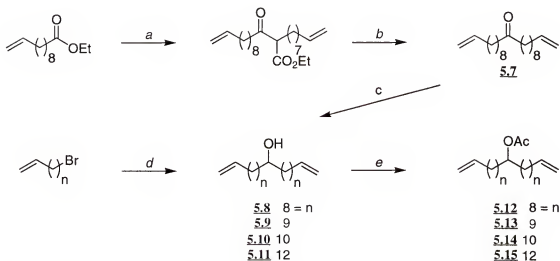


Figure 5-10. Syntheses of diene monomers with central pendant acetoxy groups. *a*: 0.5 eq KH. *b*: LiCl, DMSO, H_2O , Δ . *c*: LAH. *d*: ①Mg, ②0.5 eq HCO_2Me . *e*: AcCl or Ac_2O , pyr.

Chloro- and Phenyl-Substituted Dienes

Intermediates shown in Figure 5-10 were also converted to symmetrical dienes with central pendant chloro and phenyl substituents (Figure 5-11) from which ethylene/vinyl chloride and ethylene/styrene model copolymers may be prepared. The reported mildest method for converting alcohols to chlorides is a variation of the Mitsunobu reaction, utilizing PPh_3 , DEAD and ZnCl_2 where the nucleophile is chloride ion supplied by the zinc salt.⁹² Multiple attempts to prepare the chloride monomer **5.16** by this route proved to be low-yielding (< 40% crude yield). Combination of the products from each of the reactions yielded a practical quantity of crude monomer (~1g). However, an impurity was present in detectable (GC, NMR) amount which proved difficult to separate even by HPLC. The combination of excess Ph_3P in refluxing CCl_4 did however prove effective in converting the secondary alcohol to the chloride in good yield. Some elimination was apparent in the ^1H NMR spectrum (small broad multiplet near 5.4 ppm) of the crude product but, surprisingly, the eliminated product could be separated and the pure chloride (100% GC) was obtained after simple flash chromatography.

Dienes substituted by a phenyl ring can be used to prepare model ethylene/styrene copolymers. To this end a phenyl-substituted monomer was easily obtained from the ketone diene (**5.7**) also shown in Figure 5-11. The phenyl ring is attached via nucleophilic attack by phenyl lithium on the carbonyl carbon and the resulting benzylic alkoxide is deoxygenated *in situ* under Birch reduction-like conditions.⁹³

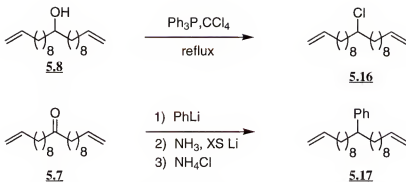


Figure 5-11. Preparation of chloro- and phenyl-substituted dienes.

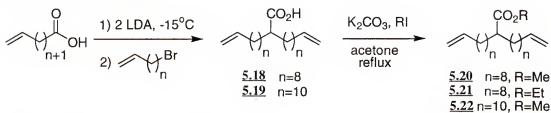
Monomers with Pendant Alkoxy-Carbonyl Moieties

Dienes with central pendant alkoxy-carbonyl groups (Figure 5-12) were synthesized as monomers for model ethylene/acrylate copolymers. One of the most useful organic transforms for constructing carbon skeletons of this type is the dialkylation of enolate ions with alkyl halides. This method has previously been shown to be effective in the synthesis of symmetrical diene intermediates for use as ADMET monomers.⁵¹ This route, was exploited to prepare the methyl substituted dienes (Figure 5-5) discussed earlier in this chapter. The diene skeleton is constructed by twice alkylating the enolate of ethyl acetoacetate, generated *in situ* by deprotonation with *t*-butoxide base. Deacylation by simple retro-Claisen reaction yields the desired ester-functionalized dienes like the target monomers shown in Figure 5-12. To convert to other esters (different R), would simply require trans-esterification or the use of a different starting acetoacetate ester.

Review of the literature indicated that this process for constructing the diene skeleton would not be effective for producing the desired larger dienes as dialkylation of β -keto esters with very long alkyl halides has been shown⁹⁴ to be a very low yielding

reaction. As an alternative, previous researchers turned to the dianions of carboxylic acids as carbon nucleophiles. These may be generated by reaction of a carboxylic acid, with α -hydrogens, with two equivalents of LDA at $0^\circ \geq T \geq -15^\circ\text{C}$ and are stable in THF solution even at 50°C for several hours.⁹⁵ Their use is not complicated by Claisen condensation type reactions, multiple sites for C-alkylation, and very low temperatures are not required for their generation or alkylation.

Acrylate-like functionality



Methyl methacrylate-like functionality

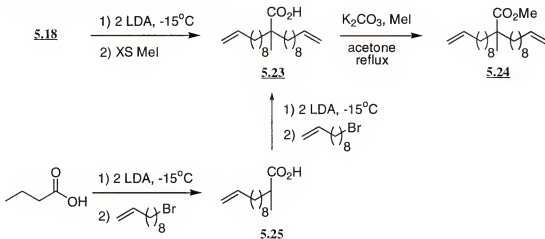


Figure 5-12. Synthesis of dienes with pendant alkoxy carbonyl functionality.

The needed long chain ω -unsaturated carboxylic acids were available in our laboratories, as they are intermediates in the synthesis of alkenyl bromides described earlier in this chapter (Figure 5-9). The synthetic scheme for preparing ester-functionalized dienes is outlined in Figure 5-12. Construction of the diene skeleton

proved to be high yielding and the products are easily purified by simple flash chromatography. The acid groups of these dienes were O-alkylated in near quantitative yields by base promoted esterification with excess methyl or ethyl iodide, which has been shown in the literature to be a particularly effective method for sterically hindered esters.⁹⁶ Classic Fischer esterification with sulfuric acid catalysis was not utilized due to the susceptibility of the olefinic groups to acid-catalyzed hydration or isomerization.

The acid dienes may also be alkylated at the α -position, via the same enolate chemistry, producing monomers with methacrylic acid-like functionality. It was reported⁹⁵ that trisubstituted acids, produced by alkylation of the enolates of disubstituted acids, could be easily purified by simple aqueous extraction. That is, the starting material could be separated from the product by simple preferential extraction of the disubstituted acid into basic aqueous solution. Hoping to capitalize on this presumed facile method, the acid diene **5.18** was methylated in the α -position. However, the starting material and the product, **5.23**, could not be separated as described by aqueous extraction. As expected due to the very small structural difference between the starting material and the product, **5.23** could not be adequately purified by practical techniques. Only after repeated small-scale HPLC purification could a satisfactory sample be obtained. A more facile approach to **5.23** involves twice alkylating the enolate of propionic acid with 9-decenyl bromide. The much larger disparity in molar mass and polarity of the starting materials and product greatly eased purification. Base-promoted O-alkylation of **5.23** then affords the desired precursor with methyl methacrylate-like functionality. The polymer which results from this monomer is yet to be prepared.

An unsymmetrical acid-functional diene, **5.26**, was constructed by this method and then deoxygenated to the corresponding methyl-substituted monomer, **5.27**, for comparison with its symmetrical counterpart prepared previously and to be published elsewhere.^{51c}

Propylene-like functionality (unsymmetrical)

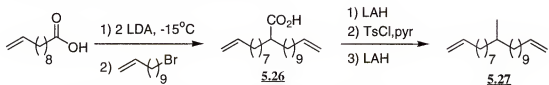


Figure 5-13. Synthesis of unsymmetrical methyl substituted monomer.

Preparation and Characterization of ADMET Ethylene/Polar Monomer Copolymers

Each of the model polymers was prepared by the one-pot homogeneous ADMET/heterogeneous hydrogenation process described in Chapter 4. The only exception, a model ethylene/vinyl chloride copolymer, required the use of a different hydrogenation system to be discussed later. Monomer and catalyst (400:1) were combined inside an argon-purged dry box and the reaction was then conducted at 45-65°C (48hrs) under reduced pressure utilizing schlenk line techniques. The resulting unsaturated polymers were combined with silica (100 times the weight of ruthenium catalyst) and olefin hydrogenation was conducted in toluene at 90°C under 120 psig H₂ for 24 hours to insure maximum reduction. The catalyst residue/silica composite was filtered from solution and the solvent evaporated under reduced pressure to yield the colorless, viscous or white solid polymers in virtually quantitative yield. The samples were not reprecipitated except where noted. Molecular weights as measured by GPC

versus polystyrene standards consistently fell within the range $2 - 5 \times 10^4$ g/mol with PDT's ~ 2 .

ADMET Ethylene/Vinyl Acetate Model Copolymers

Ethylene/vinyl acetate (EVA) copolymers constitute the world's largest volume ethylene copolymer, due in no small part to the technical significance of the post-polymerization hydrolysis to ethylene vinyl alcohol copolymers.³⁷ They are prepared by the traditional free-radical techniques employed for low-density polyethylene. This is a special case of an ideal copolymerization, termed Bernoullian, where the reactivity ratio product $r_1 r_2 \cong 1.0$ and $r_1 \cong r_2 \cong 1.0$. Monomer incorporation is truly random and the copolymer constitution is the same as the feed ratio, allowing the preparation of EVA's with a broad range of compositions. The ready availability of EVA's with varying VA content has made this copolymer system the most ideal available one for studying copolymer composition/property and morphology relationships and as a result much physical data has accumulated for these copolymers.⁹⁷ The abundance of physical data concerning random EVA's should prove most useful for later comparison with the model periodic ADMET EVA's reported here.

A series of ADMET EVA's was prepared with pendant acetate groups separated by 18, 20, 22, and 26 backbone carbons. The latter 3 polymers yield tough films and fibers from solution and from the melt and optically transparent or translucent articles may be obtained from the melt.

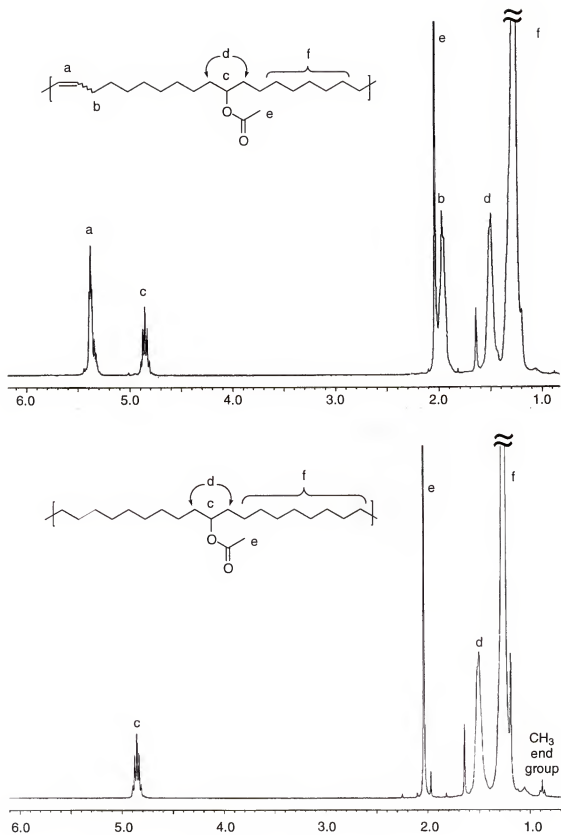


Figure 5-14. ^1H NMR spectra for **P5.12** and **HP5.12**.

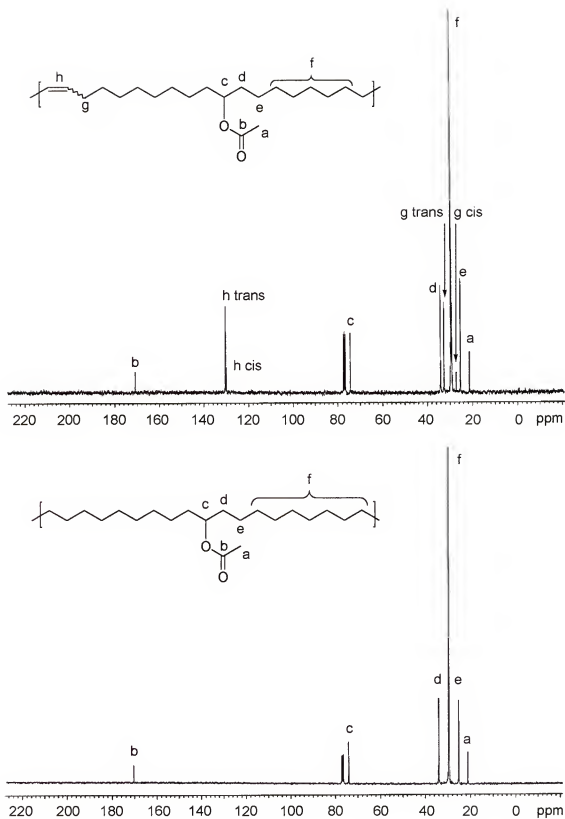


Figure 5-15. ^{13}C NMR spectra for **P5.12** and **HP5.12**.

The ^1H and ^{13}C NMR spectra for **P5.12** and **HP5.12** are shown in Figures 5-14 and 5-15. Examination of the olefin regions indicates that the method for hydrogenation is exhaustive as indicated by complete disappearance of signals at $\sim 5.3\text{-}5.4$ ppm (^1H) and at ~ 130 ppm (^{13}C). The diminutive ^1H signals at 4.9 and 5.8 ppm (terminal vinyl groups of unsaturated polymer) and at 0.8 ppm (corresponding methyl end groups of saturated polymer) indicate high molecular weight. Hydrogenation greatly simplifies the ^{13}C spectrum as a result of the degeneration of chemical environments distal to the acetate group. All spectra for the remaining EVA models are identical, regardless of ethylene run length, aside from changes in the ^1H integrals corresponding to decreasing acetate content.

The pattern of peaks in the ^{13}C spectra of the model EVA is characteristic of all the model polymers regardless of the pendant functionality. In addition to peaks attributed to the pendant group and the methine carbon, the only other peaks are a partially resolved cluster of peaks at ~ 30 ppm ("f" in Figure 5-15) and signals slightly downfield and upfield relative to "f" for the carbons α and β , respectively, to the methine carbon. The cluster of peaks "f" may be partially resolved to 3-5 peaks and corresponds to backbone carbons (polyethylene segments) more than twice removed from the methine carbon. The GPC traces of **P5.12** and **HP5.12** are overlaid in Figure 5-16 to illustrate constancy in retention time and polydispersity. The unchanged PDI suggests the absence of any reactions such as chain scission or other means of molecular weight reduction during hydrogenation. The fact that the retention time remains the same is not conclusive evidence that DP is unaffected, only that hydrodynamic volume is similar. It might however be expected that the conversion of isolated double bonds, separated by long

flexible segments to single bonds would not drastically affect hydrodynamic properties. Should this assumption hold, then it can also be assumed that identical M_p from GPC truly indicates unchanged DP. Also of note, PDI for all of these polymers will remain ~2 as opposed to much broader and variable PDI's (3 – 7) for commercial EVA's.

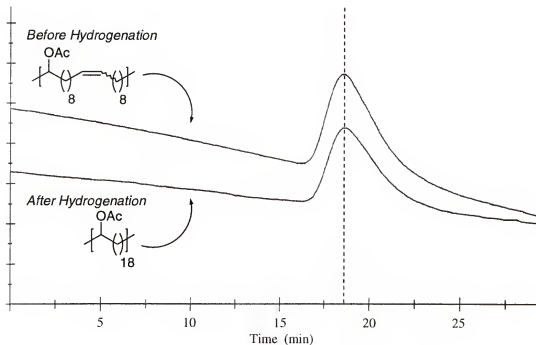


Figure 5-16. GPC traces for **P5.12** and **HP5.12**. $\overline{M}_n = 4 \times 10^4$ g/mol, PDI = 1.8.

Thermal Analysis of EVA Model Copolymers

The physical properties of EVA copolymers can be tailored by varying the VA content to fit applications as diverse as hot melt adhesives, packaging films, and rubbery toys.³⁷ Melting point depression upon inclusion of a noncrystallizable repeat unit into a crystallizable backbone is a general phenomenon and EVA copolymers are no exception, where the degree of depression is proportional to the comonomer content.

This phenomenon was treated theoretically by Flory⁹⁸ and described by the well-known Equation 5-2. The equation describes the observed melting point (T_m) as a function of the mole fraction of noncrystallizable groups (X_b) where T_m^0 is the theoretical maximum melting point of the crystalline homopolymer and ΔH_m^0 is the heat of fusion per crystallizable repeat unit. While this equation adequately describes the generally observed trends in melting point depression, it underestimates the magnitude of depression due to oversimplifying assumptions.⁹⁹ Among other things, the theory assumes crystals of infinite dimensions, ignores the chemical identity of the non-crystallizable unit, and assumes crystallization of very short segments. Subsequent revisions of the theory provide closer fit to experimental data but these versions still fall short.

$$T_m = T_m^0 \left(1 - \frac{RT_m^0}{\Delta H_m^0} X_b \right) \quad \text{Eqn 5-2}$$

Not surprisingly, the same trend in T_m (DSC) with increasing VA content was observed with these model EVA polymers. As expected, each of the polymers displayed narrow melting transitions relative to commercial EVA's due to greater chemical homogeneity. Typical DSC heating traces, with varying thermal pretreatment are shown in Figure 5-17 along with a trace reported elsewhere for a commercial EVA (28% VA wt/wt, not to scale); overlaid to demonstrate the stark contrast in melting behavior. The melting transition for this polymer spans 50°C, typical of semicrystalline random copolymers indicating a broad range of crystalline morphologies ascribed to chemical inhomogeneity.

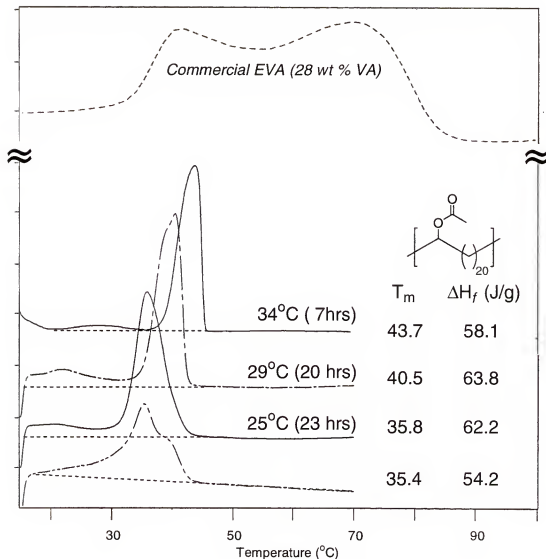


Figure 5-17. Annealing studies for **HP5.13** (24.4 wt % VA). Annealing conditions are indicated above each trace.

The samples were heated to 100°C to erase thermal history and then scanned at 5°C/min, cooling cycle first, to locate thermal transitions. On the cooling cycle, all polymers displayed a first order, sharp exotherm, generally spanning <15°C. On the heating cycle, a broader endotherm with a shoulder on the high temperature side was observed (bottom curve, Figure 5-17). The difference between the peak temperatures for

the two major transitions, assigned as T_c and T_m respectively, was $\leq 20^\circ\text{C}$. The onset of the T_m is unclear due to observed premelting indicated by the slope of the baseline leading up to the peak, which may induce error in the measured values for ΔH_m .

Annealing was found to affect the positions and shapes of the melting endotherms in typical fashion¹⁰¹ (Figure 5-17). Samples were isothermally crystallized from the melt at various temperatures (T_a) below T_m , cooled to 15°C and then scanned at $5^\circ\text{C}/\text{min}$. Some observations regarding the effect of annealing are:

- Peak T_m and ΔH_m increase with increasing T_a and the peak sharpens.
- Baseline preceding T_m changes (dotted lines included to aid visualization).
- For $T_a = 34^\circ\text{C}$, ΔH_m decreases and broad endotherm below T_a appears.

While interpretation of thermal analyses such as these in relation to polymer morphology without corroboration with other techniques (e.g., X-ray, microscopy, etc.) can be perilous, some general statements are in order. Annealing between T_m and T_c provides energy to allow amorphous polymer to organize into crystals, allows crystals to organize into larger crystals, and allows defective crystals to become more perfect. The outcome is generally an increase in T_m and/or ΔH_m as seen in the results above. The slope of the baseline preceding T_m for the unannealed sample may be the result of melting (possibly with simultaneous recrystallization) of a population of smaller or less perfect crystals formed during the thermal scan. In the annealed samples, a greater percentage of this population has most likely been more highly organized and melts at the higher temperature. Annealing at $T_a = 34^\circ\text{C}$ shifts the T_m to a still higher value but provides enough thermal energy to maintain more of the polymer in the liquid state. Poorly formed crystals can then arise during the cooling prior to scanning and these

crystals may give rise to the broad exotherm preceding the higher temperature, narrow peak.

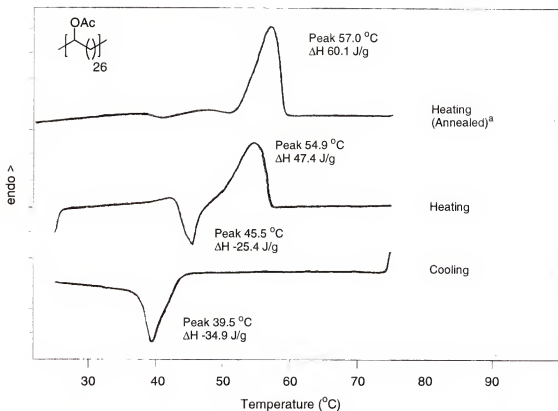


Figure 5-18. DSC trace of **HP5.15** with endotherm prior to T_m on heating indicating cold-crystallization. a: Annealed from the melt (49°C, 5 hrs)

The DSC trace for **HP5.15** reveals thermal behavior not observed with any other polymer reported in this dissertation (Figure 5-18). The endothermic peak on the heating cycle just prior to the T_m indicates cold crystallization. This phenomenon, first theoretically treated by Wunderlich,¹⁰² is most effectively observed after a crystalline polymer is quenched from above T_m to below T_g , minimizing crystallization. On heating to a given temperature between T_m and T_g , crystallization ensues. The rate of crystallization for **HP5.15** may be significantly slower than for the other EVA's, diminishing the effective crystallization which occurs during the cooling scan. On the

subsequent heating cycle, more of the amorphous material then crystallizes rapidly just below T_m . Annealing just below T_m as before for the other polymers all but eliminates the sharp endotherm in the subsequent heating scan.

The melting points (unannealed) of the polymers are plotted versus weight % VA together with the values reported¹⁰³ for the commercially available Elvax® series (Figure 5-19). Like the commercial resins, the relationship is linear ($R^2 = 0.99$) in the region studied. The values are consistently lower for the model polymers and the absolute value for the slope is approximately 3 times that of the commercial resins. It is interesting to note the relationship between the values of the y-intercepts, corresponding to 0%VA. The intercept for the commercial resins is 114°C which is very close to the reported $T_m = 110^\circ\text{C}$ for the parent low density polyethylene prepared under the same conditions. Although it may be purely coincidental, the intercept for the model EVA's (145.6°C) is almost exactly the same as the theoretical value for perfectly linear polyethylene(145.5°C).

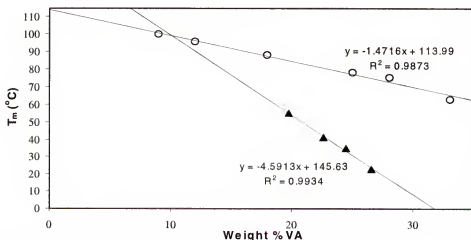


Figure 5-19. Plot of T_m vs. weight % VA. ▲ ADMET EVA copolymers (5°C/min). ○Elvax® series commercial EVA (10°C/min)¹⁰³.

Upon heating to approximately 300°C, acetic acid is thermally eliminated from the polymer backbone and this is the source of the upper limit for processing and end use temperatures of commercial EVA's. Measurement of weight loss due to this reaction by TGA has been shown to be a useful technique for measuring the acetate content of EVA copolymers.¹⁰⁴ A representative TGA plot (**HP5.12**) is shown in Figure 5-20 together with the tabulated predicted and measured % weight loss due to thermal elimination of acetic acid for each polymer. The transition between the weight loss due to thermal elimination of AcOH and the onset of further decomposition was not seen as a distinct plateau nor did it occur at the exactly same temperature for each run. The end of the first step was taken as the inflection point "A" (Figure 5-20) digitally calculated for each plot. Average values for each of the model EVA's are tabulated showing good correlation between the measured acetate content and that calculated from the known repeat unit.

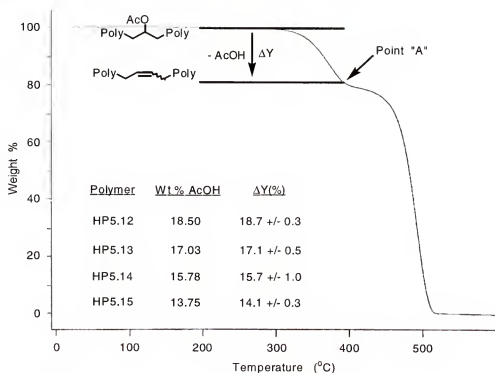


Figure 5-20. TGA trace for **HP5.12** showing typical two-stage weight loss. Values reported for ΔY are average of 3 runs.

ADMET Ethylene/Alkyl Acrylate Copolymers

Commercial ethylene/methyl acrylate (EMA) copolymers generally contain approximately 20 weight % methyl acrylate.³⁷ The monomer reactivity ratios for methyl acrylate and ethylene differ substantially ($r_1=11$, $r_2 = 0.2$, $M_1 =$ methyl acrylate) compared to the EVA system($r_1=1.02$, $r_2=0.97$, $M_1 =$ vinyl acetate) at 60°C. A plot of copolymer composition (F_1) vs feed composition (f_1) using these values for both systems is shown in Figure 5-21. The high initial slope of the line for EMA indicates that very small changes in feed ratio have a significant effect on copolymer composition in the range of copolymer composition (10-40 weight % comonomer) typical for useful properties in EVA. In this range, a change of 1% in f_1 results in approximately 5% change in F_1 .

EMA's exhibit similar physical properties to EVA's which is not surprising considering that the pendant groups in the polar repeat units are merely isomers, differing only in the orientation of the ester group. Technical bulletins put forth by Chevron make numerous comparisons between their EMAC® series of ethylene/methyl acrylate copolymers with commercial EVA copolymers. Reported melting points for the EMAC® resins are within 10°C of the analogous EVA (Elvax®, DuPont) resins with approximately the same weight percent comonomer.

The DSC heating curves for HP5.20 are HP5.22 are shown in Figure 5-22 along with the analogous ADMET EVA's for comparison. In agreement with the commercial relatives, DSC thermal data for the ADMET EVA's and EMA's do not show drastic differences in peak melting temperatures. However, distinction is seen in the shape of the

endotherms where the EMA peaks appear narrower and do not exhibit a high temperature shoulder as seen in the latter.

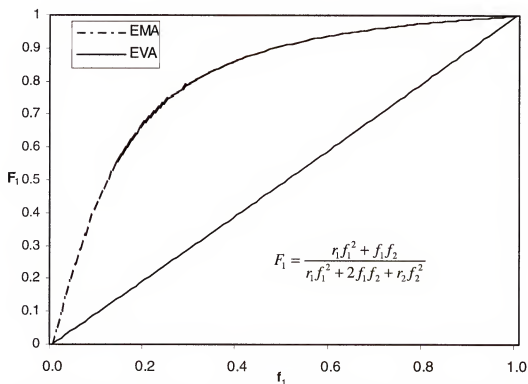


Figure 5-21. Dependence of copolymer composition (F_1) on comonomer feed composition (f_1) for EMA and EVA.

Without corroborative evidence, we can only speculate at this point as to the cause of this difference. While no attempts were made to measure second order transitions here, it has been shown that commercial EVA's and EMA's exhibit significantly different second order transitions attributed to flexible side-group reorientation. Numerous studies, empirical¹⁰⁵ and theoretical,¹⁰⁶ reach the general consensus that the cause is greater hindrance of rotation of the pendant ester group of MA relative to VA repeat units about the bond by which each is attached to the main chain.

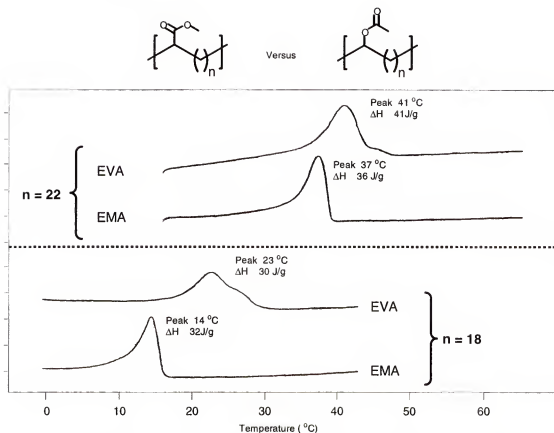


Figure 5-22. DSC heating curves for ADMET EMA's and EVA's (2nd scan 5 $^{\circ}\text{C}/\text{min}$)

Comparison of representative partial ^1H NMR spectra (Figure 5-23) of the EVA and EMA models in the region of the methine protons reveals the differing chemical environments exerted by the two groups on the proximal backbone atoms. The methine proton of the EVA gives rise to the expected pentet due to splitting by four equivalent geminal protons. However, in the case of the EMA, these four protons are not equivalent due to anisotropy induced by the attached carbonyl, supporting theoretical calculations indicating greater hindrance to rotation. Perhaps the differing mobilities of these two pendant groups affects crystal packing in these periodic polymers giving rise to the observed differences in melting behavior.

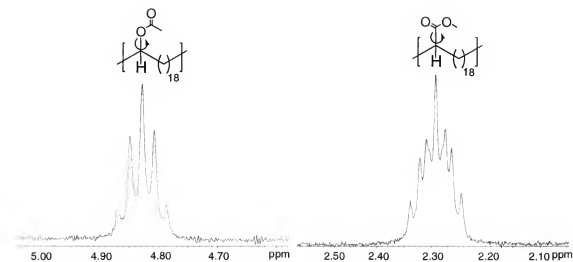


Figure 5-23. Partial ^1H NMR spectra of ADMET EVA and EMA showing differing multiplicities of methine proton signals.

A significant difference exists between the thermal stabilities of commercial EVA's and EMA's, with important technical implications, where the lower thermal stability of the former limit their maximum processing temperatures to 232°C, nearly 100°C lower than for the latter. TGA measurements bear out the expected higher thermal stability of the ADMET EMA's with T_d (10% Wt loss) \cong 445°C, and with an onset approximately 100°C greater than for the EVA's.

The larger ethoxycarbonyl group of **HP5.21** (ethylene/ethyl acrylate, EEA) causes a significant change in the profile of the DSC melting endotherm (Figure 5-24) relative to the analogous EMA. Two maxima are seen and the position of the higher temperature maxima is within 1°C of the peak seen for the analogous EMA model. Annealing at 3°C(1hour) shifts the lower temperature maxima by nearly 4°C toward the higher temperature peak, creating greater overlap and eliminating visible premelting as evidenced by flattening of the slope of the baseline prior to the endotherm. It might be assumed that incorporation of the larger ethoxy carbonyl group into some type of ordered

array is more difficult than the smaller methoxy carbonyl. Although based solely on speculation, the observed melting behavior of the EEA and EMA might suggest that similar morphologies are formed in both with more of a less perfect phase in the EEA giving rise to the lower temperature peak. Annealing just below this lower temperature peak shifts it to higher temperature possibly indicating crystal perfection toward that giving rise to the higher temperature peak.

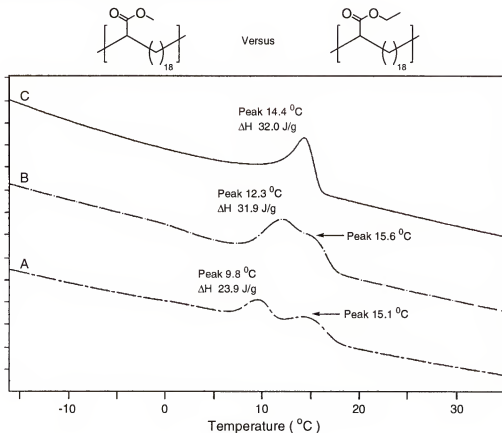


Figure 5-24. DSC heating traces for ADMET EMA(HP5.20) and EEA(HP5.21).
A: EEA, B: EEA annealed 3°C(1hr), C: EMA.

ADMET Ethylene/Styrene Model Copolymer

Due to the extremely high reactivity of styrene relative to ethylene, copolymers with even moderate levels of ethylene incorporation are unattainable by free-radical

copolymerization. Alternately, traditional Ziegler-Natta copolymerization of ethylene and styrene typically produced polymers which contain less than 1% styrene.¹⁰⁷ Recent reports disclose the use of homogeneous half-sandwich and metallocene catalysts, activated by MAO, to successfully prepare ethylene/styrene copolymers with varied levels of styrene content.¹⁰⁸

In order to compare the effect of a regularly spaced phenyl group on crystallization, an ADMET ethylene/styrene copolymer (**HP5.17**) was prepared. Much larger melting point depression is seen relative to the analogous EVA copolymer with 18 carbons between pendant groups. Figure 5-25 shows the DSC heating trace with two broad but apparently separate endotherms with low ΔH relative to other polymers. Annealing for 5 hours between the two peaks resulted in a relatively broad peak at approximately -6°C with several maxima following the peak temperature. The obvious assumption in this case is that the greater steric bulk of the phenyl ring has a drastic effect on the packing behavior of the polymer chains.

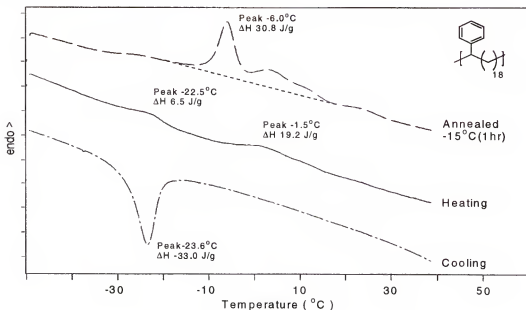


Figure 5-25. DSC traces for ADMET E/STY (**HP5.17**).

ADMET Ethylene/Vinyl Chloride Copolymer

Chlorinated polyethylene (CPE) may be prepared from polyethylene via various chlorination techniques resulting in polymers with are formally ethylene/vinyl chloride (EVC) copolymers.¹⁰⁹ These materials have significant technical possibilities and have proven convenient subjects for microstructure/morphology studies.¹¹⁰ In particular, morphological studies have been aimed at determining whether the chloride groups are included into crystal lattices as defects or excluded in amorphous regions. In an elegant study by Wegner,^{110a} EVC's were prepared by several chlorination techniques from PE and partially hydrogenated polyoctenamers. The different methods produced polymers with varying incorporation of isolated and vicinal chloro substituents. X-ray studies in concert with DSC measurements indicated that the chloro groups were incorporated as defects in the crystals. As the chloride content of the polymers increased, the lateral dimensions of the unit cell were shown to increase relative to the unit cell of pure polyethylene. Polymers with vicinal chloro groups showed greater melting point depression as a result of the larger defects. Alternately, EVC's with a broad range of chlorine content have also been prepared by partial reduction of PVC with trialkyl tin hydrides and similar results were obtained from X-Ray and DSC measurements.^{110c}

The DSC melting points of random EVC's were compared to analogous ethylene/propylene (EP) copolymers as a function of counit content and the two data sets fell on the same line.^{110b} The researchers concluded that the melting behavior was the same due to the similar size of the chloro and methyl groups. The smaller van der Waals radius¹¹¹ of chloride (1.75 Å) relative to methyl (2.0 Å) may be offset somewhat by the longer C-Cl bond length (1.78 Å) relative to C-C (1.54 Å).

In order to compare the effect of a periodic chloro group to the other pendant groups in this study, an ADMET ethylene/vinyl chloride (EVC) copolymer was prepared. The EVC could not be prepared by the one-pot method used for all the other polymers in this study. While the ADMET reaction proceeded in high conversion utilizing the ruthenium catalyst, the heterogeneous hydrogenation step never proceeded to greater than 70% (^1H NMR). It is postulated that the chloride acts in some fashion to poison the heterogeneous hydrogenating species. However, hydrogenation over Pd/C at 5 atm H_2 in toluene proved quantitative within spectroscopic detection limits. The reduction was conducted at 40°C as the polymer begins to precipitate from room temperature toluene during the course of the reaction as evidenced by the formation of gelatinous particles in the mixture. Subsequent observations showed the final product to be poorly soluble in toluene, benzene, methylene chloride, and 1,2-dichloroethane but freely soluble in chloroform and THF at room temperature.

Based purely on steric arguments, a model ethylene/vinyl chloride copolymer with pendant chloride every 19th carbon would be expected to have a higher melt than any of the analogues reported here with the same ethylene run length. This was indeed found to be the case as **HP5.16** shows a $T_m = 77^\circ\text{C}$ ($\Delta H_m = 78 \text{ J/g}$). In stark contrast to the studies involving random EVC and EP,^{110b} the analogous ADMET EP polymer with a pendant methyl every 19th carbon melts 21°C lower ($T_m = 56^\circ\text{C}$)^{51c} than this ADMET EVC.

TGA shows stepwise weight loss due to thermal elimination of HCl prior to catastrophic decomposition. The elimination of HCl occurs at a lower temperature than for loss of AcOH from EVA, consistent with the relative stabilities of secondary alkyl

chlorides and acetates. The measured weight loss due to elimination of HCl (11.54 %) is in reasonable agreement with that predicted from the known structure (12.11 %).

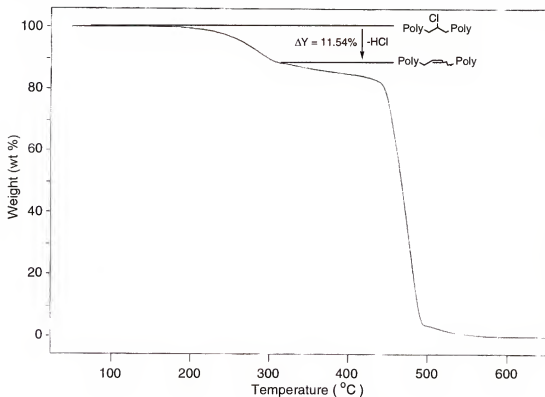


Figure 5-26. TGA trace of **HP5.16**. Onset for catastrophe decomposition = 445°C.

Conclusions

The method of homogeneous ADMET/heterogeneous hydrogenation has been demonstrated as an effective and facile alternative to two step procedures for the generation of models for ethylene polar monomer copolymers. The necessary dienes are easily prepared by typical organic transforms whereby the type of substituent in the polymers and their frequency in the backbone is regulated during the monomer synthesis. Access to periodic polymers with much longer ethylene run lengths than previously

reported was made possible through the synthesis of homologated ω -alkenyl bromides and carboxylic acids used in the diene synthesis.

Comparison of polymer melting behavior of a series of polymers with identical ethylene run lengths but differing pendant groups R, found correlation between the degree of melting point depression and the steric bulk of R with the highest degree of depression for R = phenyl and the lowest for R = Cl. The trend is graphically depicted in Figure 5-27. In addition to precisely defined run lengths, all the model ethylene polar monomer copolymers regardless of comonomer, have approximately the same molecular weights and PDI's, decreasing the number of variables which must be considered for adequate analysis of physical data. Enormous potential for obtaining deeper insight into structure property relationships of commercial ethylene/polar monomer copolymers via more applied property studies of these models is at hand.

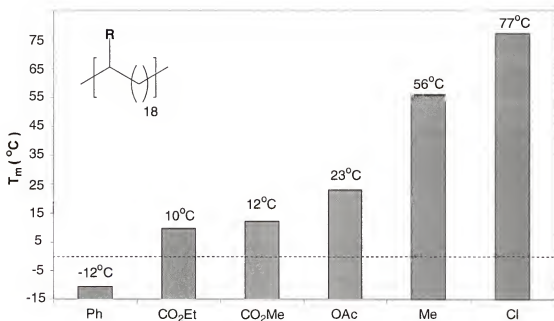


Figure 5-27. Peak melting temperatures of ADMET ethylene/polar monomer copolymers as a function of chemical identity of the regular pendant group. Value for R = Ph is the average of two observed peaks.

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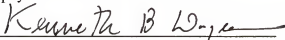
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BIOGRAPHICAL SKETCH

Mark Deas Watson was born on February 23, 1969 in Pascagoula, Mississippi. Shortly thereafter, he moved with his parents and five older siblings as they reestablished residence in their hometown, Hattiesburg, MS. Upon graduation from Oak Grove High School in 1987, he entered the University of Southern Mississippi enrolling in the Department of Polymer Science. He conducted undergraduate research in various facets of solution phase properties of surfactants and polymeric viscosity modifiers under the guidance of Prof. Robert Y. Lochhead. He also participated in a cooperative education program with Schering-Plough in Memphis, Tennessee where he spent three alternating semesters in the Dr. Scholl's Materials and Devices R & D. After receiving his B.S. degree in August 1992, he remained at USM for one year conducting research in the Shelby F. Thames group in the area of formulation and physical testing of adhesives and coatings. He began his graduate studies in organic/polymer chemistry at the University of Florida in August 1993 under the guidance of Professor Kenneth B. Wagener. During a brief visit home in March 1996, he met his wife-to-be, Kim, whom he married in August of the following year. Mark received his Ph.D. in May 1999, and began post-doctoral research at the Max-Planck-Institut für Polymerforschung in Mainz, Germany in the research group of Prof. Dr. Klaus Müllen.

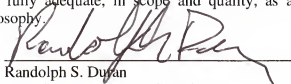
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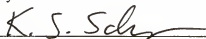
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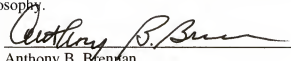
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Anthony B. Brennan
Associate Professor of Materials
Science and Engineering

This dissertation was submitted to the Graduate Faculty of the Department of Chemistry in the College of Liberal Arts and Sciences and to the Graduate School and was accepted as partial fulfillment of the requirements for the degree of Doctor of Philosophy.

May, 1999

Dean, Graduate School